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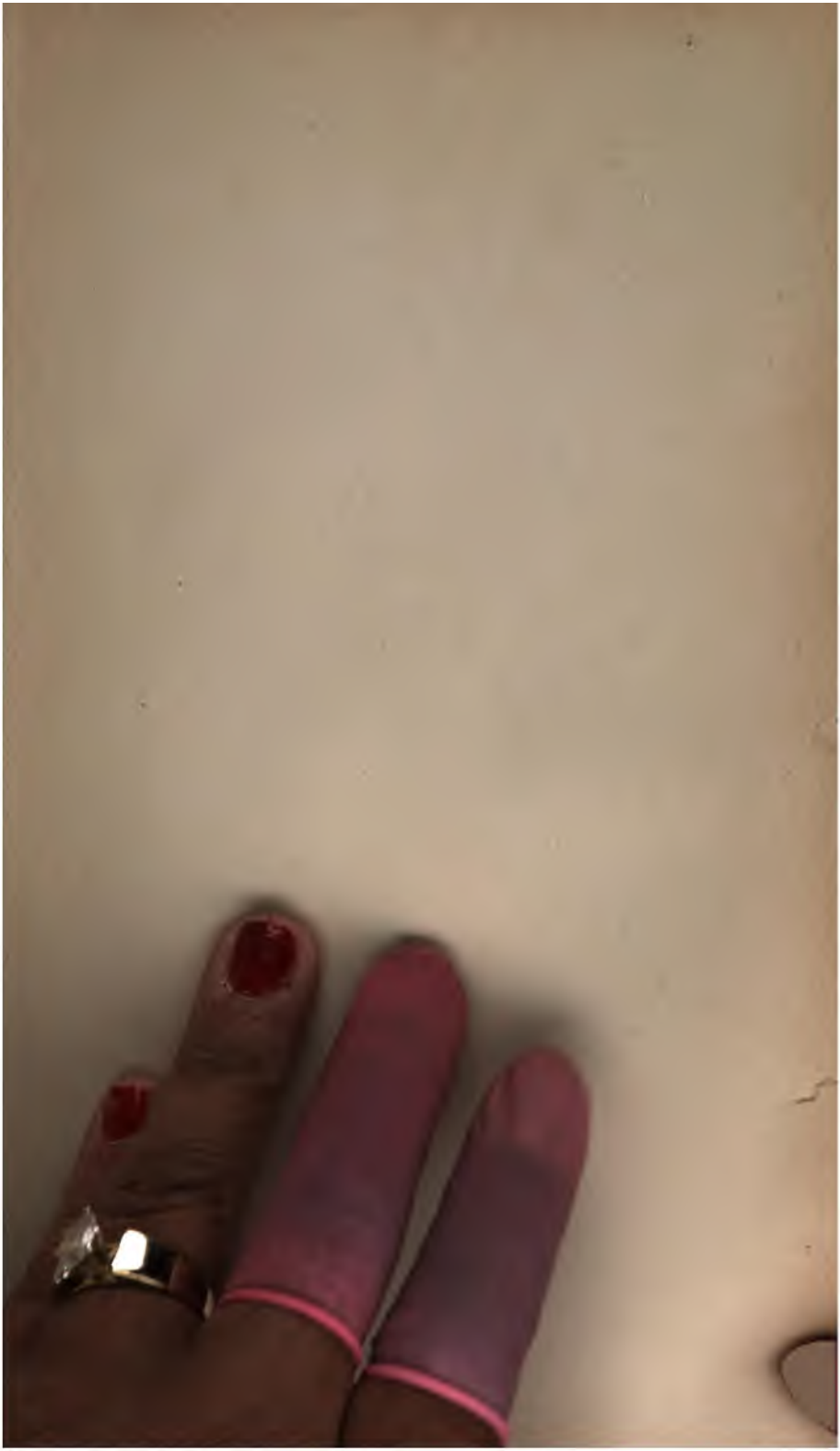

(Percy)

VIN.

METALLURGY.

SILVER AND GOLD.—Part I.

METALLURGY:

THE

ART OF EXTRACTING METALS FROM THEIR ORES.

By JOHN PERCY, M.D., F.R.S., F.G.S.,

LECTURER ON METALLURGY TO THE ADVANCED CLASS OF
OFFICERS OF THE ROYAL ARTILLERY;
AND HONORARY MEMBER OF THE INSTITUTION OF CIVIL ENGINEERS,
OF THE SOCIETY OF ENGINEERS, AND OF THE
IRON AND STEEL INSTITUTE.

SILVER AND GOLD.—Part I.

WITH NUMEROUS ILLUSTRATIONS ON WOOD, MOSTLY FROM ORIGINAL DRAWINGS.

LONDON:
JOHN MURRAY, ALBEMARLE STREET.
1880.

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BY THE SAME AUTHOR.

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PREFACE.

Of all the branches of Metallurgy, that of which Silver forms the subject is, in my opinion, the most extensive, the most varied, and the most complicated. Nevertheless, I hoped, when I began to write on this subject now more than ten years ago, that it would not extend beyond a single volume of moderate size, especially as the volume on the Metallurgy of Lead which I published in 1870 contains much relating to the Metallurgy of Silver. But, as I proceeded in my work, I found it impossible to do justice to the subject in such a volume. Accordingly, it became necessary to deviate from my original plan, and I now propose to devote two volumes to the kindred subjects of Silver and Gold, which are so closely allied that they cannot be separately treated.

Much of the next volume is already in type; and, as I have recently resigned my office at the Royal School of Mines, I have much more time at my disposal, and shall, if health continue, be able, I hope, speedily to complete my task. I may here state that while I regret my resignation on account of the pleasure which I derived from the performance of my duty as Lecturer on Metallurgy, I have reason to rejoice that I am no longer subject to the *quasi*-military autocratic rule of the science branch of the Department of Science and Art at South Kensington.

Owing to the changes that have taken place during the last few years in chemical nomenclature, which is still in a transitional state, the student of modern metallurgical memoirs and treatises is apt to be not a little perplexed; but I have tried as far as possible to meet that difficulty by introducing the different terms now current.

I have gratefully to acknowledge the valuable assistance which I have received from metallurgists at home and abroad in the preparation of this volume; and it will be seen that in the text I have invariably mentioned the names of the friends who have thus aided me. But I must not omit to state here how

much I feel indebted to my excellent friend Mr. J. G. Hochstaetter Godfrey, for his gratuitous, laborious, and persevering co-operation throughout a large part of this volume. Mr. Godfrey, *né* Hochstaetter, a German by birth, but now a naturalized Englishman, is settled in London as a professional mining engineer and metallurgist. He formerly worked in my laboratory, and his name frequently appears in my volume on the Metallurgy of Iron and Steel. Afterwards he was engaged for six years in copper mining and smelting in Cuba, and subsequently, for a similar period, officiated as Mining Engineer-in-chief to the Japanese Government.

In conclusion, I beg to express an earnest hope that my former students and other metallurgical friends will continue from time to time to provide me with information concerning what they have observed and the metallurgical processes in which they may be engaged.

JOHN PERCY.

London, January, 1880.

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*** *The formulæ within black brackets are those according to the atomic weights now current.*

ERRATA.

Page 33. The statement in the paragraph beginning with "mercury also attacks, etc." does not agree with that in p. 32, but the discrepancy is not mine.

„ 76. The reader is requested to cancel the record of experiment No. 5, an error having been detected in the mode of analysis, owing to the use of ammonia-water; and the results of some of the other similar experiments in which this reagent was employed are also inaccurate. A new and careful investigation concerning the action of cupric and cuprous chloride on sulphide of silver has been made in my laboratory, a report of which will appear at the beginning of the next volume, in the article on the Theory of the Patio Process.

„ 83, line 14. The statement in the paragraph beginning with "*Remarks*" is not correct.

METALLURGY.

SILVER.

HISTORICAL NOTICE.

This beautiful metal was in use and even current as money in the most ancient historic times. Abraham paid Ephron in silver for the land which he bought for the burial-place of his family.[1] Pliny laments the lavish applications of silver in his day, and regards them as a proof of luxury and demoralization. Thus he writes: "Et quid haec attinet colligere, cum capuli militum, ebore etiam fastidito, caelentur argento, vaginae catellis, baltea lamnis crepitent, jam vero paedagogia in transitu virilitatis custodiantur argento, feminae laventur et nisi argentea solia fastidiant eademque materia et cibis et probris serviat! * * * Heu mores! Fabrici nos pudet."[2] "And to what purpose collect these [instances of the lavish use of silver], since the sword-hilts of soldiers, ivory even being despised, are inlaid with silver, scabbards jingle with chains and belts with plates [of silver], even pages as they are approaching manhood are protected by silver,[3] women bathe and despise baths not of silver, and the same material is applied to serving food and to foul purposes. * * * Alas for manners! Fabricius puts us to shame."

PHYSICAL PROPERTIES OF SILVER.

Colour.—Silver when in a compact mass is remarkable for its whiteness, and by that quality alone an experienced eye will distinguish it from nearly every other metal or alloy. Amongst the common metals tin and cadmium most resemble it in colour; and, amongst the rarer, indium and lithium; the latter of which, according to Bunsen, equals silver both in colour and brilliancy, so as to render it impossible in those respects to distinguish one from the other.[4] In

NOTE.—*Where reference is made simply to the "Jahresbericht," it applies to the series of volumes commenced, under the editorship of Liebig and Kopp, in* 1847.

[1] Genesis, ch. xxiii. 15, 16.

[2] Naturalis Historiæ, lib. xxxiii. cap. xii. sect. 54, Sillig's edition. 1851. v. 5. p. 120.

[3] See Celsi Medicinæ, lib. vii. cap. 25. By means of a clasp passed through the foreskin, "sometimes for the sake of the voice, and sometimes for the sake of health."

[4] Chemical Gazette, 1855. 13. p. 185.

the state of extremely fine powder it is grey and earth-like, but immediately acquires its characteristic metallic lustre under the burnisher; and when an ingot, obtained by fusion under certain conditions hereafter to be mentioned, is broken in two cold, as it may easily be, the fractured surfaces are white as snow. A more beautiful fracture of its kind than this cannot well be imagined.

Lustre.—It is capable of receiving a most brilliant polish.[5]

Crystalline system and structure.—It crystallizes in the cubical or regular system. The product termed "Blicksilber" by the Germans, which is described in the preceding volume by the Author on the Metallurgy of Lead (p. 196), occasionally presents a manifestly crystalline structure on its fractured surface; and in cavities in the same product Hausmann observed regular octahedra. The same author possessed two beautiful and sharply-defined octahedra, of which the largest measured on the sides of its triangular faces 1½ Paris line (*i.e.* about 3 mm.); they were found in the solidified drops of silver hanging on the sides of a crucible from which molten silver had been poured at the Vienna Mint.[6]

A bar of fine silver, of about 1000 oz., 4·75 in. wide at the top, 3·5 in. at the bottom, 4·0 in. thick, and 12·0 in. long, after having been nicked across the middle of the bottom to the depth of about 0·75 in., was supported at each end and then broken slowly by hydraulic pressure applied to the upper surface, immediately over the nick upon the lower surface. It proved to be very tough, and was bent nearly into the form of a right angle before breaking. The fracture was

---

[5] A. Vogel recommends the use of ferric oxide, prepared by the calcination of ferrous oxalate, as preferable to ordinary levigated colcothar, as a polishing powder for glass lenses, metals, etc., especially for the finer work. (Chem. Gaz. 1854. 12. p. 410.) The following receipt for preparing polishing powder may be interesting to some persons. It was communicated to the Society of Arts in May 1833, by Mr. A. Ross, of Clerkenwell, and will be found in the Transactions of the Society. The oxide of iron, which is sold under the names of *colcothar of vitriol*, *crocus*, *tripel*, or *rouge*, contains much extraneous matter, which, owing to its having nearly the same specific gravity as the oxide of iron itself, cannot be removed from the latter by levigation. Crystals of ferrous sulphate are to be dissolved in water, and the solution filtered, in order to separate siliceous particles, which are said to be generally present, and sometimes abundant. To the filtered solution a saturated solution of soda [neutral carbonate?] is added, and the precipitate thereby produced is to be repeatedly washed and then dried, after which it is very gradually heated in a crucible to dull-redness, and poured, while hot, into a clean metal or earthen dish: on cooling it absorbs oxygen from the atmosphere, and acquires a beautiful dark-red colour; in which state it is fit for polishing the softer metals, such as silver and gold, but will scarcely make any impression on hardened steel or glass. To fit it for polishing the harder substances, it must be heated to bright redness, and kept so until it acquires a deep purple hue when exposed to the air. After this treatment it must be rubbed with a wrought-iron spatula on a wrought-iron slab, and afterwards levigated in a very weak solution of gum-arabic. Thus prepared, the oxide is "almost impalpable," is free from all extraneous matter, and is eminently suitable for polishing steel, glass, the softer gems, etc.

Care should be taken to forbid the use of any powder for polishing silver which contains metallic mercury. Such powders are, however, sold to butlers for that purpose; and though it may save those persons time and trouble, yet it is needless to remark that it must increase the wear of the silver plate.

[6] Beiträge zur metallurgischen Krystallkunde, von Joh. Friedr. Ludw. Hausmann. Abhandl. d. Königl. Gesellschaft d. Wissenschaften zu Göttingen, 1850. B. 4.

dead-white, uneven or hackly, fibrous at the sides and bottom, but not at the top,—the direction of the fibres being at right angles to those surfaces,—and elsewhere granular. Here and there were a few small bright cavities, unequally distributed. Under a lens the granular part of the metal seemed to be confusedly crystalline. I have pleasure in acknowledging the kindness of my friends Messrs. Johnson, Matthey, & Co., for permitting this experiment to be made at their works.

Mr. Richard Pearce, formerly manager of the Morfa Silverworks, at Swansea, at my request fractured a large ingot of silver, whilst hot, in the following way:—Melted silver was poured into an open cast-iron ingot-mould of the usual trapezoidal cross-section. The ingot was broken by the blow of a hammer: it was 2·4 in. wide at the top, and 2·0 in. wide at the bottom, and 0·9 in. thick. Within an area approximating to the segment of a circle, of which the chord was formed by the upper edge of the fracture, commencing at about half an inch from each end, the metal consisted of a confused aggregation of imperfectly formed octahedral crystals; while the rest of the fracture was largely fibrous or columnar, with the fibres nearly at right angles to the sides and bottom of the ingot.

Hardness.—The statement usually met with in books, that silver is harder than gold and softer than copper, has been confirmed by the experiments of Calvert and Johnson, who by means of a machine, specially constructed for the purpose, found the hardness of gold, silver, and copper to be in the ratio of 4 : 5 : 7·2.[7] It is scratched by copper. A bar of silver emits a dull sound when struck. As Karsten rightly remarks, "silver voice" and "silver tone" are poetical expressions.[8]

Malleability and ductility.—It is said that in these qualities it is only exceeded by gold, that it may be hammered into leaves $\frac{1}{10000}$ of an inch thick, and that a single grain may be drawn out into a wire of 400 feet long. It is hardened by hammering or rolling, but recovers its malleability by annealing at a low red-heat.

Specific gravity.—Gustav Rose found it to be 10·5036 after fusion, 10·57 after striking the metal in a coining press, and from 10·5485 to 10·6139 in the finely-divided state in which it is thrown down from an aqueous solution of its nitrate by the addition of sulphate of protoxide of iron.[9] Wertheim gave the sp. gr. of pure silver cast into an ingot as 10·366; of silver cold-hammered and drawn out as 10·369, and of the same after rupture by stretching as 10·320; and of silver cold-hammered, drawn out and annealed as 10·304, and of the same after rupture by stretching as 10·193. Wertheim's experiments were made at a temperature of from 12° to 13° C.[1] Langsdorf found 10·429 to be the sp. gr. of well-annealed silver wire.[2] Berzelius gave the sp. gr. of silver as varying from 10·474 and 10·542;[3] and Karsten as

[7] Wagner's Jahres-Ber. 1859. 5. p. 108.
[8] System der Metallurgie, 5. p. 467.
[9] Chemical Gazette, 1848. 6. p. 136. Jahresber. 1847-1848. p. 38.
[1] Ann. de Chim. et de Phys. 3. s. 1844. 21. p. 415.
[2] Handwörterb. d. rein. u. angewandt. Chem. 1859. 7. p. 892.
[3] Traité de Chimie. Paris, 1846. 2. p. 476.

between 10·40 and 10·50, and after having been hammered and rolled as 10·70.[4] Matthiessen found the sp. gr. of pure silver drawn out into wire about $\frac{1}{8}$ in. thick to be 10·468 at 13·2° C.[5] Professor Cooke of Cambridge, U.S., has found the sp. gr. of pure silver, cast in a small bar, to be 10·469 at 0° C.; and of the same bar, after being rolled thin and annealed, 10·505.[6] Christomanos, Professor of Chemistry in the University of Athens, found the sp. gr. of pure silver, which he had distilled, to be 10·575.[7] Roberts has found the sp. gr. of pure silver while molten to be 9·461.[8]

Tenacity.—According to Baudrimont, the tenacity of silver wire of 1 square millimetre (= 0·016 square inch) of sectional area at 0° C., 100° C., and 200° C., is 28·324, 23·266, and 18·577 kilogrammes, respectively,[9] *i.e.* 17·27, 14·19, and 11·33 tons per sq. in. respectively. Wertheim has published the results of experiments upon the tenacity of silver under different conditions in the following tabular form; the diameter of the wire operated upon appears to have been 1·772 mm. (=0·0709 in.).

TABLE SHOWING THE RESULTS OF WERTHEIM'S EXPERIMENTS ON THE TENACITY OF SILVER.

Tenacity of	At 10° to 15° C.		At 100° C.	At 200° C.
	Rupture slowly produced.	Rupture suddenly produced.		
(in kil. per sq. mm.)				
Silver wire, drawn out	29·00 kil.	29·60 kil.	—	—
" " annealed	16·02 "	16·40 "	14·00 kil.	14·00 kil.
(in tons per sq. inch)				
Silver wire, drawn out	17·69 tons	18·05 tons	—	—
" " annealed	9·77 "	10·00 "	8·54 tons	8·54 tons

A wire $\frac{1}{10}$ inch in diameter is stated by Aikin to support a weight of about 240 lbs. without breaking:[1] this is equivalent to about 13·64 tons per sq. in. of sectional area.

Specific heat.—According to Dulong and Petit it is 0·0557 from 0° C. to 100° C., and 0·0611 from 0° C. to 300° C.;[2] whereas, according to Regnault, it is 0·05701 from 0° C. to 100° C.[3]

Dilatation by heat.—By Troughton 0·000020826 is given as the coefficient of linear dilatation, *i.e.* the extension per unit of length for 1° C. from 0° C. to 100° C.;[4] by Lavoisier and Laplace (silver re-

[4] System der Metallurgie, 1832. 5. p. 467.
[5] Wagner's Jahres-Ber. 1861. 7. p. 116.
[6] Communicated to the Author.
[7] Fresenius' Zeitschrift für analytischen Chemie, 1868. 7. p. 301.
[8] Proceedings of the Royal Society, 1875. 23. p. 493.
[9] Ann. de Chim. et de Phys. 3. s. 30. p. 304.
[1] Diction. of Chemistry and Mineralogy, 1807. 2. p. 311.
[2] Jamin, Cours de Physique, 1859. 2. p. 374.
[3] Claudel, Formules, 1864. p. 397.
[4] Jamin, op. cit. 2. p. 13.

fined by cupellation) 0·0000190974;[5] by Matthiessen 0·00001943:[6] by Fizeau (silver which had been fused) 0·00001936.[7] Thus the dilatation may be taken as equal to 0·002 from 0° C. to 100° C., or $\frac{1}{500}$ of the length. According to Roberts the mean coefficient of linear dilatation between the ordinary atmospheric temperature and 1050° C., when the metal is molten, is 0·00003721, and that of cubic dilatation 0·00011164.[8]

Melting-point.—The results of different observers are discordant, as might be anticipated from the different modes of estimating temperature which they adopted. The melting-point of silver was given by Pouillet as 538° C. (=1000·4° Fahr.),[9] but in a later edition of his work on physics it is given as 1000° C.[1] Guyton-Morveau gave it as 1033·71° C.[2] Prinsep gave it as 999° C.[3] By means of a thermo-electric pyrometer of platinum and palladium Becquerel found 960° C. to be the melting-point of silver;[4] and he ascertained that silver did not actually melt at the temperature of the vapour of zinc evolved from the metal boiling under ordinary atmospheric pressure, though it became so much softened at that temperature as to cause separate pieces of silver, in contact with each other, to stick together.[5] Now H. Sainte-Claire Deville determined that the temperature of the vapour of zinc, so evolved, is about 1040° C.[6]; whence it may be inferred that the melting-point of silver somewhat exceeds that temperature; and this I am disposed to regard as nearest the truth.

Latent heat.—Person gives the latent heat of fusion as 21·07.[7]

Conductivity for heat and electricity.—Silver has a higher conductivity for heat and electricity than any other metal, and has, therefore, been adopted as the standard and as equal to 100. Hard-drawn silver wire has a lower conducting power for electricity than the same wire after annealing: if the conductivity of the hard-drawn wire be taken as 100, that of the annealed wire will be 107, according to Becquerel; 108·8, according to Siemens; and 110, according to Matthiessen.[8]

Volatilization by heat.—Silver is quickly volatilized in the arc of a powerful voltaic current, and boils when heated before the oxyhydrogen blowpipe or in the flame of coal-gas and oxygen. According to Stas the vapour of silver produced by ignition of the pure metal in this flame is pale blue, slightly inclining to purple, and not green as has been recorded. The green tint which has been observed is due, Stas maintains, to the presence of copper. By means of the same flame and a little apparatus consisting of lime, he has succeeded in distilling silver in considerable quantity.[9] According to Roberts

[5] Claudel, op. cit. p. 388.
[6] Phil. Trans. 1866. 156. p. 868.
[7] Compt. rendus, 68. p. 1125.
[8] Op. cit. p. 494.
[9] Élémens de Physique, 1832. 1. p. 318.
[1] 7th edition, 1856. 1. p. 265.
[2] Ann. de Chimie, 1814. 90. p. 236.
[3] Phil. Trans. 1828. Part I. p. 94.
[4] Jahresber. 1863. p. 25.
[5] Idem, p. 74.
[6] Ann. de Chim. et de Phys. 3. s. 58. p. 293: see also Compt. rendus, 56. pp. 981–2.
[7] Ann. de Chim. et de Phys. 1848. 3. s. 24. p. 276.
[8] On an Alloy which may be used as a Standard of electrical Resistance. Phil. Mag., Feb. 1861.
[9] Nouvelles Recherches sur les Lois des Proportions chimiques, etc. Par J. S. Stas. Mémoires de l'Académie Royale des Sciences, des Lettres et des Beaux-arts de Belgique, 1865. tome 35.

and Lockyer, "the vapour of silver when condensed into fine particles, escaping into an atmosphere of hydrogen, is blue by reflected light."[1] Berthier states that when silver is subjected in a charcoal-lined crucible to the high temperature of a porcelain furnace (*i.e.* in which hard porcelain, or porcelain properly so called, is fired), it loses about 0·005 of its weight, or a little less than copper under the same conditions.[2] According to A. D. Van Riemsdijk, Assistant-Assayer at the Dutch Mint, silver, heated in a slow current of hydrogen, begins to volatilize, in a sensible degree, at a temperature not much above the melting-point of copper, which he assigns as 1330° C.; and, in support of this statement, he adduces the results of experiments by himself, which seem to have been very carefully made.[3]

According to A. Parkes, "silver is easily volatilized when in connection with zinc and arsenic in a fused state" (*sic*). He secured the application of this alleged discovery in a patent, sealed Sept. 11, 1851. Silver is thus to be separated from metallic copper, from copper regulus, etc. The operation is directed to be conducted in a reverberatory furnace, "having a flue and chambers connected therewith, suitably arranged for collecting the products that pass from the furnace; and, when so collected, they may be cupelled, or otherwise treated, to obtain the silver"![4] In the volume on the Metallurgy of Lead by the Author, a process is described for separating zinc by volatilization in a blast-furnace from the argentiferous zinc, containing lead, produced in Parkes' process of desilverization. But if silver can be so easily volatilized by means of zinc, as Parkes alleges, the process in question can hardly be deemed satisfactory. Malaguti and Durocher experimented upon this subject, and found that by heating in a retort a mixture of roasted argentiferous blende and charcoal, and collecting the zinc distilled therefrom, the latter contained only traces of silver.[5] (See Alloys of Silver and Zinc in the sequel.)

Transmission of light.—The film of silver deposited on glass by Liebig's process is so thin that when it is held up to bright sunlight it appears transparent and of a beautiful blue colour.[6]

According to Léon Foucault, thinly-silvered glass (*Silberspiegel*) transmits a portion of the light falling upon it, and that portion has a bluish colour; and he has shown that this is a case not of porosity but of passage through the actual substance of the metal.[7] Christomanos states that light transmitted by extremely thin silver-leaf is bluish-green, and by somewhat thicker ones, yellow to yellowish-brown.[8]

Other physical properties.—Silver is tasteless and odourless.

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[1] Proceedings of Royal Society, 1875. 23. p. 344.
[2] Tr. des. Ess. 2. p. 776.
[3] Archives Néerlandaises, 1868. vol. 3.
[4] Chemical Gazette, 1852. 10. p. 219.
[5] Recherches sur l'Association de l'Argent aux Minéraux Métalliques, etc. Paris, 1850, p. 27. (Reprinted from the Annales des Mines for 1850.)
[6] Handwörterbuch der Chemie, 1859. 7. p. 902.
[7] Jahresber. 1866. p. 75.
[8] Fresenius' Zeitschrift, 7. p. 29).

Brittle Silver.

Church has examined a silver ornament brought by General de Cesnola from an ancient tomb in the island of Cyprus, which, it is believed, was at least 1500 years old. The ornament was in the form of a crescent, with the ends thin and pointed, and the middle much stouter: it consisted of three portions:—(*a*) An outer crust, $\frac{1}{30}$ of an inch thick, which could be removed by the finger-nail: it was composed of finely-divided metallic silver, with traces of sulphide and chloride of silver, copper, apparently in the form of basic carbonate, and a trace of gold.

(*b*) The mass of the substance, which was white, metallic, highly lustrous, and uniform, but extremely brittle.

(*c*) A core of unaltered ductile metal, existing only in the thicker part of the crescent.

It is remarkable that *b* and *c* had *precisely* the same composition, which was as follows:—

	Per cent.
Silver	94·69
Gold	0·41
Copper	3·43
Lead	0·28
Antimony with traces of arsenic and bismuth	1·21
	100·02

Church, therefore, attributed the brittleness of *b* "to a molecular change, which, in the course of ages, had occurred throughout all the thinner parts of the piece of silver, but had left unchanged in the thickest part a central fusiform core. A crypto-crystalline structure had been produced in the previously homogeneous alloy, which caused the peculiarly easy fracture of the metal. A smart blow with a hammer was capable of shattering it to powder, while by rolling or gentle hammering, the brittle mass could be restored readily to its pristine condition. The density of the brittle silver was 9·06, but, by rolling, it became 10·20." This is an interesting case of physical change in a metal, apparently not caused either by vibratory or concussive action, or great alternations of temperature.[9]

Warington examined an ancient silver vase about 0·016 of an inch thick, taken out of brick-earth near London; it had become very brittle and highly crystalline. Under a microscope, magnifying 100 diameters, the facets of the crystals were exceedingly bright and apparently cubical, but none of them were perfectly developed; there was a thin layer of chloride of silver on the surface, so that possibly the crystals had pre-existed and been merely disclosed by the slow etching action of the chlorine derived from some chloride existing in the soil; the brittleness was removed by heating to redness for a few minutes, whereby the metal became compact and granular in structure, and its sp. gr. was increased from 9·937 to

[9] Chem. News, 1871. 23. p. 243.

9·950. The percentage composition of the metal with the thin layer adherent is given in I., and Church infers that without the layer it would have been as stated in II.:[1]—

	I.	II.
Silver	90·01	96·74
Copper	2·83	3·03
Gold and loss	0·33	0·23
Chloride of silver	6·12	..
Sesquioxide of iron	0·71	..
	100·00	100·00

Further observations relating to this subject will be found recorded under the head of Modes of Formation of Chloride of Silver.

CHEMICAL PROPERTIES OF SILVER.

Atomic weight.—Ag = 108 [idem].—According to Stas it is 107·929.

SILVER AND OXYGEN.

Silver is not acted upon at ordinary temperatures by oxygen, whether dry or moist; but molten silver has the property of absorbing oxygen, which it afterwards gives off during solidification. It is a question whether this is a case of simple absorption or, as Plattner inferred, one of actual chemical combination. If the latter, it is quite anomalous, because oxide of silver is immediately reduced when heated *per se* to a much lower temperature. When silver is deflagrated by the electric discharge in atmospheric air, vapour is produced which condenses in the form of brown powder stated to be oxide of silver. By heating silver before the oxyhydrogen blowpipe H. Sainte-Claire Deville and H. Debray produced large quantities of oxide of silver. Proust also had oxidized silver before a simple mouth-blowpipe, and more recently oxide of silver is reported to have been found in the condensed fumes from blast-furnaces in which argentiferous lead (*plomb argentifère*) was treated.[2]

Dioxide or Suboxide of Silver, Ag^2O [Ag^4O].

Wöhler has investigated this oxide and certain of its salts. When oxalate, mellitate, or citrate of protoxide of silver is heated in a current of hydrogen to 100° C. or somewhat higher, yellow or brown salts of the dioxide are formed. The dioxide is precipitated as a black powder from solution of the citrate by potash, and in a dry state acquires metallic lustre by burnishing. When, according to Weltzien, clean silver foil is dipped into a perfectly neutral solution of peroxide of hydrogen, it becomes at first covered with bubbles of oxygen, and then with a grey-white layer of mono-hydrated argentous oxide. The reaction is shown in the following equation:—

$$2Ag + HO^2 = Ag^2O,HO.$$
$$[4Ag + H^2O^2 = Ag^4O,H^2O.]$$

[1] Mem. and Proc. of the Chem. Soc., 1845. 2. p. 47. Chemical News, 1871. 23. p. 253.

[2] Comptes rendus, 1875. 80. p. 459.

The argentous oxide dissolves, and a small quantity of a grey-blue substance is precipitated. When this solution is exposed to the air, it acquires the colour of salts of protoxide of cobalt, and becomes slightly turbid, owing to the separation of finely-divided silver; hydrate of potash throws down from it a brown-black substance, and hydrochloric acid, a mixture of chloride of silver and metallic silver; by evaporation a residue is left, which under the microscope appears crystalline, and from which water dissolves hydrated argentous oxide, while silver, in microscopic translucent red crystals, remains; the solution of argentous hydrate, so produced, has a feebly alkaline reaction, and yields, on the addition of hydrochloric acid, argentic chloride.[3] By heat argentous oxide is resolved into oxygen and silver;[4] but according to Lenssen it may, in combination with certain other oxides, exist at a high temperature. He states that on melting in a crucible a precipitate consisting of the sulphides of silver, zinc, and iron, with nitre and carbonate of soda, he found above the button of silver an olive-coloured crust, upon the surface of which was a lake-coloured fine powder, composed as shown in the following formula:[5]—

$$Fe^2O^3 + Ag^2O + 7ZnO.$$
$$[Fe^2O^3 + Ag^4O + 7ZnO.]$$

Faraday published the following observations on the behaviour of oxide of silver, precipitated either by one of the alkalies or of the alkaline earths, and dissolved in ammonia; a pale brownish solution being thereby produced. If this solution is exposed to the air in an open vessel, a brilliant pellicle forms on its surface, and this, when removed, is succeeded by others, until most of the metal is separated. It is grey by reflected light, and bright yellow by transmitted light. The precipitate is an oxide of silver, and was noticed by Berthollet (in the first volume of the Annales de Chimie), who ascribed its production to the evaporation of ammonia. Faraday found that the mean of many analyses of the precipitate gave 157·4 of silver, and 7·5 of oxygen, which nearly corresponds to the formula Ag^8O^3 [$Ag^{16}O^5$]. When heated gradually, the oxide is reduced, giving off oxygen without change of form; but when heated suddenly, it fuses first, and leaves a solid button of silver. H. Vogel considers that the substance obtained by Faraday was a mixture of argentous and argentic oxides, and that the former resulted from the action of light.[6]

Protoxide or Oxide of Silver, AgO [Ag^2O].

It may be conveniently prepared by the addition of lime- or baryta-water to an aqueous solution of nitrate of silver, washing the precipitate so formed, and heating to 100° C., at which temperature it is perfectly desiccated.[7] It is hardly necessary to remark that the

[3] Jahresber. 1866. p. 261.
[4] Gmelin's Handb. 6. p. 139.
[5] Jahresber. 1862. p. 227.
[6] Idem, p. 229.
[7] H. Rose, Chemical Gazette, 1852. 10. p. 182. It is stated in the Handwörterbuch der Chemie, 7. p. 961, that this oxide is perfectly desiccated at a temperature of 60° to 70° C., and gives off some oxygen at 100° C.

precipitant should be entirely free from chlorine. Soda or potash may be used instead of lime or baryta; but they should be free from carbonic acid as well as chlorine. Thus obtained, oxide of silver is a deep brown powder of an olive tint, and is stated to have a sp. gr. of 7·143. According to H. Rose, pure oxide of silver is grey-brown, and blackens in sunlight.[8] By adding to a solution of 1 gramme of nitrate of silver in 15 grammes of water pure hydrate of soda, dissolved in 20 parts of water, then dropping in ammonia-water until the precipitated oxide of silver was dissolved, and afterwards diluting with water, the solution, according to H. Vogel, became coated with a brilliant violet-coloured film, which darkened on exposure to light; and which film, under the microscope, was found to consist of an aggregation of star-shaped crystals of protoxide of silver, with three, four, and six rays: these crystals appeared to belong to the cubical system. After a few weeks the precipitation of oxide of silver ceased.[9] It begins to lose oxygen at 250° C.[1]; and is wholly reduced at a temperature sensibly below redness, without, as I have clearly ascertained, showing the least sign of fusion. Berthier states that "it is very fusible;"[2] an error which, if not typographical, is unaccountable on the part of an observer so generally accurate. It is completely reduced when mixed with charcoal at a temperature below that at which *per se* it evolves oxygen. [See the report of experiments, made on this subject in my laboratory, in the volumes by the Author, published in 1861 and 1875, under the head of Reduction by Carbon.] It is said to evolve oxygen on exposure to solar light. In association, or, as it is supposed, in combination, with certain other metallic oxides, such as those of lead, copper, and manganese, it ceases to be completely reducible by heat alone.[3] It is a powerful base, and while moist turns red litmus paper blue, and turmeric paper brown.[4] According to Bineau, water dissolves about $\frac{1}{3000}$ of its weight of oxide of silver, and the solution decomposes not only haloid salts, but also oxysalts, setting free the metallic bases in the state of oxide.[5] Oxide of silver dissolves in an aqueous solution of ammonia or carbonate of ammonia in excess, of hyposulphite of soda, of cyanide of potassium or sodium, and of the cyanides of the so-called alkaline earthy metals. It is not soluble in an aqueous solution of potash, soda, or baryta. When oxide of silver is boiled in a solution of chloride of sodium, decomposition occurs, chloride of silver is formed, and the solution becomes strongly alkaline; and when water is added to the solution after cooling, considerable turbidity is produced, owing to the deposition of chloride of silver. In an experiment on this reaction it was found that, after the solution had remained in a glass flask during several days, the surface of the glass was skinned off by the action of the caustic soda which had been produced. The deposited chloride was washed and digested

[8] Ausführliches Handbuch der analytischen Chemie, 1851. 1. p. 168.
[9] Jahresber. 1862. p. 227.
[1] H. Rose, op. antea cit.
[2] Tr. des Ess. 2. p. 778.
[3] Idem, p. 779.
[4] A. Vogel, Jahresber. 1871. p. 338.
[5] Compt. rendus, 1855. 41. p. 509.

vith nitric acid, to which it yielded protoxide of silver in very mall quantity, the original protoxide experimented upon having been nearly wholly changed into chloride. In another similar experiment relatively less protoxide of silver was operated upon; and after boiling for some time, nearly the whole of the oxide was hanged into chloride and dissolved, chloride of silver depositing on ooling. (C. Tookey, in my laboratory, 1869.) According to Wetzlar, when at ordinary temperatures moist oxide of silver is added to an queous solution either of chloride of potassium or sodium, so long as t becomes white, a caustic solution of the alkali is obtained, which is quite pure;" and yet, in a note, he adds that on neutralizing the iltered solution with nitric acid, or adding thereto chloride of sodium, urbidity is produced, owing to the precipitation of chloride of silver. do not understand why either of these reagents should have produced the effect stated if the alkaline solution had been "quite pure."

Wetzlar found that by shaking an aqueous solution of phosphate f soda with oxide of silver until its colour remained unchanged, the olution became strongly alkaline, but retained a considerable quantity f phosphoric acid.[6]

It forms apparently definite compounds with ferrous oxide, and vith the same oxide in association with ferric oxide; but these will e more suitably described in the sequel, in the article on Nitrate of ilver, where the action of ferrous sulphate on that nitrate is considered. Compounds of it and of some other oxides have also been roduced, as will be seen in the sequel.

When oxide of silver is heated to redness with chloride of ammonium, both metallic silver and chloride of silver are produced. By he first action of the heat a portion of the oxide is reduced to netallic silver, which is not altered by the chloride of ammonium. The remainder of the oxide is converted directly into chloride.[7]

Oxide of silver, freshly precipitated and while still moist, readily bsorbs carbonic acid from the atmosphere.

According to H. Rose, there is no hydrate of oxide of silver, or at east none which can exist at 100° C.[8]

According to Böttger, ignition takes place when dry oxide of ilver is triturated with sulphide of gold, black sulphide of antimony, ealgar, orpiment, milk of sulphur, selenium, amorphous phosphorus, annic acid, or creosote.[9]

According to Malagnti and Durocher, oxide of silver is pretty asily reduced by mercury, the silver separated amalgamating with he mercury in excess.[1] Fischer asserts that when perfectly pure xide of silver, free from any trace of a salt of silver, especially arbonate of silver, is dissolved in water, it is reduced by zinc, admium, tin, lead, and copper; but not by iron, nickel, or cobalt,

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[6] Schweigger's Jahrbuch der Chemie nd Physik, 1828. 23. p. 99.
[7] H. Rose, Chemical Gazette, 1848. 6. . 412.
[8] Op. antea cit.
[9] Jahresber. 1863. p. 284.
[1] Recherches sur l'Association de l'Argent, etc., 1850. p. 474.

nor by the other metals which precipitate metallic silver from solutions of soluble salts of silver.[2]

Oxide of silver dissolved in ammonia-water is, according to Fischer, rapidly and completely reduced by zinc, copper, and arsenic; more slowly by cadmium, mercury, tellurium, and lead; to a slight extent by manganese and antimony; and not at all by bismuth, tin, iron, nickel, etc.[3]

Behaviour of Oxide of Silver towards the Solutions of various Metallic Salts.—According to Persoz, when protoxide of silver is boiled with an aqueous solution of nitrate of cobalt, nickel, cerium, cadmium, manganese, or copper, it dissolves, being converted into nitrate and precipitating each of those metals, respectively, in the state of oxide.[4]

The following observations on this subject were made by H. Rose.

Salts of manganese.—When a solution of sulphate of protoxide of manganese is treated, at the ordinary temperature, with moist oxide of silver, the latter soon becomes black, and the manganese is precipitated from the solution; the black substance is stated to contain argentous oxide and manganic oxide; if prepared in the cold and washed with cold water, it contains Ag^2O [Ag^4O], Mn^2O^3 [idem], together with $2AgO$ [$2Ag^2O$]; when heated somewhat in the liquid, and afterwards washed with hot water, it acquires a darker brown colour, and becomes $Ag^2O + Mn^2O^3$ [$Ag^4O + Mn^2O^3$]. This latter compound may be best produced by adding sulphate of protoxide of manganese to an excess of an ammoniacal solution of sulphate or nitrate of silver.[5]

Sulphate of cobalt.—Excess of oxide of silver throws down the whole of the cobalt from sulphate of cobalt in the state of oxide; but if moist oxide of silver be digested with an excess of a solution of that sulphate, it gradually becomes deep-black, and is converted into a compound of $AgO + Co^2O^3$ [$Ag^2O + Co^2O^3$], which however, when well washed, retains some insoluble basic sulphate of cobalt. This compound is most easily obtained by adding a little ammonia to mixed solutions of sulphate of cobalt and nitrate of silver, when, at first, there is formed a greenish-blue precipitate, which becomes quite black in the course of time, and then the compound above described is produced. The tendency of protoxide of cobalt to pass into the higher oxide, at the expense of the oxygen of the oxide of silver, is far less than that of protoxide of iron, or even protoxide of manganese.

Sulphate of nickel.—The nickel is only partially precipitated by oxide of silver, either at ordinary temperatures or by boiling. The solution of sulphate of nickel, with the addition of oxide of silver, retains its colour, though much oxide of silver may be dissolved and much oxide of nickel be precipitated.

Sulphate of cadmium.—The cadmium is only partially precipitated

[2] Op. cit. p. 117.
[3] Idem.
[4] Introduction à l'Étude de la Chimie moléculaire, par J. Persoz. 1839. pp. 361–367.
[5] Jahresber. 1857. p. 253.

as oxide by oxide of silver at ordinary temperatures, but is wholly precipitated on boiling.

Sulphate of zinc.—The whole of the zinc is precipitated as oxide by oxide of silver at ordinary temperatures. Between the oxides of these metals there is a certain amount of affinity, but it is difficult to obtain definite compounds of the two oxides. If to a solution of sulphate of zinc so much hydrate of potash be added as to redissolve the oxide of zinc at first thrown down, and then nitrate of silver, so that the liquid separated from the resulting precipitate may still contain both oxide of zinc and hydrate of potash, a precipitate is formed, less brown in colour than pure oxide of silver; its composition varies according as the solutions are more or less diluted.

Salts of lead.—The lead is wholly precipitated as oxide by oxide of silver from a solution of chloride of lead, but only partially from a solution of acetate or nitrate of lead. Between the oxides of silver and lead there is an affinity similar to that between the oxides of silver and zinc. The compound which was long since obtained by Wöhler, may also be produced by thus precipitating with oxide of silver. It is yellow, but readily becomes blackish, and, though always yellow, varies in composition according as either of the oxides predominates in the solution, and as the degree of dilution is greater or less. The compound discovered by Wöhler was prepared by the following process:—A solution of nitrate of silver and nitrate of lead,—the latter being in excess,—is dropped into a solution of caustic potash, so that the oxides may be precipitated. The precipitate is further treated with the potash solution, when oxide of lead dissolves, but there remains a perfectly insoluble compound, which is yellow, blackens in the light, and when heated to redness evolves oxygen, the residue consisting of a mixture of oxide of lead and metallic silver in such proportions as to show that a compound had been formed of the formula $AgO + 2PbO$ [$Ag^2O + 2PbO$].[6]

Salts of copper.—The whole of the copper is precipitated as oxide by oxide of silver from a solution of chloride (cuprous chloride), sulphate, or nitrate of copper. Thus copper may be separated from a solution of nitrate of silver containing it, and Rose recommends this method, on account of its simplicity, in preference to most of the known processes for effecting such separation.

Salts of mercury.—The whole of the mercury is precipitated as oxide by oxide of silver from a solution of mercuric chloride. A solution of mercuric nitrate, with a little oxide of silver, gives a white crystalline precipitate of double argentic and mercuric nitrate; but with an excess of oxide of silver, the whole of the mercury is precipitated as mercuric or red oxide. If a solution of mercuric sulphate in dilute sulphuric acid be treated with oxide of silver at ordinary temperatures, the first addition of it causes a separation of yellow basic mercuric sulphate; but by the addition of a larger quantity of oxide of silver, all the mercury is thrown down as mer-

[6] Berzelius, Jahres-Bericht, 1839. p. 147.

curic oxide; the precipitate, however, contains sulphuric acid in the form of a basic salt, which is only completely decomposed by the long-continued action of oxide of silver and repeated stirring. If dry basic mercuric sulphate be treated with moist oxide of silver, it can only be entirely decomposed by boiling. By the action of moist oxide of silver on mercurous chloride or calomel, chloride of silver and mercurous oxide or black oxide of mercury are formed, which oxide is partially resolved into metallic mercury and mercuric oxide. From a solution of mercurous nitrate mercury is precipitated as mercurous oxide by oxide of silver, but whether wholly or partially is not stated.

Perchloride of gold.—A solution of potassio-chloride of gold is immediately decolorized by moist oxide of silver, with the formation of a precipitate of chloride of silver and oxide of gold, mixed with oxide of silver.

Sulphate of oxide of chromium and alumina.—From a solution of this salt prepared in the cold, the whole of the chromium is precipitated as oxide by oxide of silver. If the solution be mixed, at the ordinary temperature, with an excess of potash sufficient completely to redissolve the oxide of chromium at first thrown down, and nitrate of silver be then added to this solution, in such proportion that a large quantity of free potash still remains in solution, the precipitate formed consists wholly of oxide of silver; but this solution of oxide of chromium in potash contains chromic acid.

Nitrate of bismuth.—From a solution of nitrate of bismuth in weak nitric acid oxide of silver precipitates all the bismuth as oxide. A compound of oxide of silver and oxide of bismuth could not be produced.[7]

Peroxide of Silver, AgO^2 [Ag^2O^4].

It is formed in the electrolysis of salts of silver, and, though of much scientific interest, it has none in relation to metallurgy, and will, therefore, not be described here.[8]

Absorption of Oxygen by Molten Silver.

The cause of the phenomenon of "spitting," which silver presents during solidification after the completion of the process of refining by lead, and which has been fully described under the head of Cupellation (see the preceding volume by the Author on the Metallurgy of Lead), was discovered by Mr. Samuel Lucas, of Sheffield, who addressed a letter on the subject to Dalton, dated May 31, 1815, which was read before the Literary and Philosophical Society of Manchester, March 6, 1818, and published in the Memoirs of the Society in the following

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[7] Chemical Gazette, 1857. 15. p. 365 et seq.

[8] A full account by Mahla of its properties and of the mode of preparing it will be found in the Jahresbericht for 1852, p. 423: see also the Handwörterbuch der Chemie, 1859. 7. pp. 962, 963.

year.[9] Lucas demonstrated by experiment that the cause was oxygen, which is absorbed by exposing pure molten silver to the action of atmospheric air, or of certain oxidizing substances, such "as some of the nitrates," and which is evolved with "ebullition" as the metal cools, whether slowly or quickly. When a large quantity of molten silver is melted so as to acquire oxygen, and then left gradually to cool, protuberances, like miniature volcanic cones, continue to be thrown up by the escaping oxygen here and there over the surface of the metal, during a quarter or half an hour, or longer. When, on the contrary, it is cooled rapidly by being poured into water, the same phenomenon occurs, but the protuberances are much smaller, and spread more equally over the surface. Lucas poured a few pounds at a time of silver, after cupellation, into a vessel containing about 30 gallons of water, and collected the gas evolved in an inverted bottle previously filled with water; and he suggests that, notwithstanding the precautions he took, some atmospheric air may have got into the bottle. The gas was sent to Dalton, who found it to contain 86% or 87% of oxygen by volume. Lucas ascertained that substances having a powerful affinity for oxygen abstracted it from silver while molten; thus, by spreading charcoal for a few moments only on the surface of the silver, the whole of the oxygen was taken from it, and there was no emission of gas during cooling, whether slowly or quickly effected.

Chevillot, in 1820, published a confirmation of the accuracy of the results of Lucas with respect to pure silver, reduced from the chloride, and silver alloyed with copper, of the respective standards 990 and 995; *i.e.* parts by weight of silver per 1000 of alloy. Silver of the standard 952 did not evolve gas in sensible quantity; and he supposed that silver of the standard 980 or 985 was the highest at which that phenomenon would occur.[1]

Gay-Lussac in 1830 communicated a short note upon the subject. He passed a current of oxygen during about half an hour through a strongly-heated porcelain tube containing molten silver, and at the instant of solidification observed that a considerable quantity of oxygen gas was disengaged. He projected nitre in small portions on silver kept melted in a clay crucible for about half an hour, and then plunged the crucible under a bell-jar filled with water in the pneumatic trough. After the lapse of a second, a large quantity of oxygen gas was tumultuously evolved. In one experiment the volume of gas was to that of the silver as 22 : 1. When the metal is allowed to fall drop by drop into the water, large bubbles of gas escape.[2] Gay-Lussac considered the evolution of oxygen from silver during solidification to be analogous to what Pelletier asserted with respect

[9] Memoirs of the Literary and Philosophical Society of Manchester, 2nd series, 1819. 3. p. 271. Plattner states that Gay-Lussac was the first to establish the cause of the phenomenon of "spitting;" but that is an error, as will be seen from the dates of papers on the subject stated above. See Plattner's Röstprozesse, p. 123.

[1] Ann. de Chim. et de Phys. 1820. 13. p. 299.

[2] Idem, 1830. 45. p. 221.

to silver and phosphorus, namely, that silver at the moment of solidification gives off half of the phosphorus which it had taken up while molten. [It gives off the whole, as will be subsequently shown.]

In order to remove any impurities in silver precipitated from its chloride by bars of zinc, I have had recourse to nitre in operating upon several thousand ounces of silver. The precipitated metal was washed with boiling water, drained, and dried. The dry precipitate was moistened with an aqueous solution of nitre, so as to add about 5% of dry nitre to the silver, and the mixture was dried. The solution was quickly absorbed by reason of the porosity of the precipitate. The dried mixture of silver and nitre was melted in small portions at a time in large Stourbridge-clay crucibles, and the melted metal was skimmed and cast into open iron ingot moulds duly prepared. During solidification copious effervescence took place from the whole surface of the silver. The ingots when cold were extremely brittle, and exhibited the most beautiful snow-white fracture conceivable; but on being simply re-melted and cast, no effervescence occurred on cooling, and sound tough ingots of pure silver were obtained. Every particle of the precipitated silver is by the foregoing treatment surrounded with matter capable of yielding highly oxidizing gas on the application of heat; and it does not seem possible by any other kind of process more thoroughly to bring every particle of the silver under the influence of oxygen at a high temperature.

According to H. Rose, if pure silver is melted under a layer of common salt or potash, 3 or 4 inches thick, the metal solidifies with a bright surface, showing that oxygen had not been absorbed and afterwards emitted; but if a little nitrate of potash or of soda is thrown upon the saline covering, and the crucible slowly cooled, "spitting" occurs. When chloride of silver is reduced by being heated with an alkaline carbonate, "spitting" does not take place, and yet during the process oxygen as well as carbonic acid is evolved: thus,

$$AgCl + KO,CO^2 = Ag + KCl + CO^2 + O.$$
$$[2AgCl + K^2CO^3 = 2Ag + 2KCl + CO^2 + O.]$$

The reason assigned by Rose is that reduction takes place at a temperature below the melting-point of silver, and that, consequently, the oxygen has escaped before the fusion of the silver. For the same reason, it is stated, chlorate of potash, KO,CLO^5 [$KClO^3$] does not cause "spitting," while chromate of potash does; the latter requiring a higher temperature for the expulsion of its oxygen than the former. Silver does not "spit" after fusion under a mixture of common salt and oxide of manganese, MnO^2 [idem].[3]

Russell and Matthiessen passed hydrogen, nitrogen, carbonic acid, carbonic oxide, oxygen, and atmospheric air through molten silver; but no "spitting" followed, except with the last two gases.[4]

Influence of gold on the "spitting" of silver.—Silver may be alloyed

[3] Poggendorff's Annalen, 68. p. 283. Chemical Gazette, 1846. 4. p. 484.
[4] Phil. Mag. 4. s. 1862. 23. p. 84.

a considerable portion of gold, even to one-third of its weight, out losing its power of absorbing oxygen while molten, and of itting" during solidification. But when gold is present in much er proportion, this phenomenon does not take place; and the wing experiment by Levol may be cited in proof. Wishing to luce an alloy of gold and silver in the ratio 2Au : Ag [idem], he ted 709·6 gram. of gold, and then added 390·4 gram. of pure silver. gold was solidified by contact with the silver; and when, after her heating, the metallic mixture had become liquid, it was stirred a clay rod in order to mix the two metals well together, when movement "instantly caused effervescence, which was so brisk, even violent, that a notable portion of the molten mass was pro-ed into the furnace, notwithstanding the mouth of the crucible several centimetres above the surface of the metallic bath." explanation suggested by Levol, and which is doubtless correct, hat after both metals had become liquid, the silver, on account of sp. gr. being much lower than that of gold, had for the most part ained as a layer over the latter, and so had had the opportunity absorbing oxygen; and that on stirring the mixture, the alloy ilting had not the power of holding the oxygen which had been en up by the silver.[5]

Occlusion of Oxygen and certain other Gases by Silver at a red-heat.

For the following interesting results we are indebted to ham. Pure silver heated to redness in oxygen gas absorbed, and ined when cold (i.e. *occluded*), 0·545 of its volume of oxygen. e silver wire, 0·002 in. in diameter, yielded 0·289 of its volume gas, consisting chiefly of carbonic acid. Graham supposed t the occluded gas might have been oxygen, and that "the er was converted into carbonic acid at the temperature of ex-ation by a trace of carbon existing in the fine silver." When ndard silver (*i.e.* an alloy containing 7·5% of copper) is heated to redness in atmospheric air or oxygen, it becomes almost black on surface from oxidation of the copper. Silver wire thus blackened s found to have occluded several times its volume of oxygen. In experiment on this point, much of the superficial oxide disap-ared; and Graham remarks, "It appeared as if the operation ded to the reduction of the superficial oxide of copper, oxygen ng liberated, and the copper absorbed by the mass of silver." A cimen of silver reduced from the oxide, in the state of sponge, in ee experiments, was found to occlude 6·15, 8·05, and 7·47 times its ume of oxygen, respectively, without any visible tarnish on the face. Silver in leaf, weighing 12·5 gram. (there were 500 leaves), ted to redness in air, was found to occlude 1·37 of its volume of ygen, 0·20 of nitrogen, and 0·04 of carbonic acid. Fine silver wire, ted to redness in hydrogen, and cooled in that gas, occluded 0·211

[5] Ann. de Chim. et de Phys. 1853. 3. s. 39. p. 167.

of its volume. The metal acquired a beautiful frosted appearance on the surface: and by repeated heating, it became highly crystalline and brittle.'

The preceding statements are not concordant. I sought an explanation from Mr. W. C. Roberts, who assisted Mr. Graham with his experiments, and have received the following remarks in reply:—"I always viewed with suspicion," says Roberts, "the large volume of oxygen occluded by the silver leaf, and by the silver reduced from the oxide, of which Mr. Graham was careful to remark that 'it was considered pure, but not analysed, and he even suggested that the high results might be due to the presence of copper."

Action of Oxygen on finely-divided Silver at a red-heat.

Plattner published a statement on this subject, which is so remarkable as to deserve particular attention, and a detailed account of the evidence on which it is founded.[6]

Finely-divided silver was carefully mixed in a glass mortar with an equal bulk of finely-triturated quartz, and the weight of the silver operated upon was 3 grammes. The mixture was put into a tube of difficultly fusible glass, ½ in. in diameter, and about 2 ft. long; and that part of the tube where the mixture lay was surrounded with platinum foil, in order that it might be more equably heated. A current of dry oxygen gas was passed through the tube during an hour; while that part of the tube containing the mixture was kept heated to moderate redness over an Argand spirit-lamp. Very soon a slight sublimate of greyish white colour appeared in the tube, near the mixture on the side furthest from the entrance of the gas. It gradually increased and extended several inches in the tube; and afterwards that portion of the sublimate which was nearest the mixture formed an annular metallic mirror. The sublimate was examined, and found to be metallic silver. The inner surface of the tube, in contact with and adjacent to the mixture, was coloured yellow; and the lower portion of the quartz, which had been most strongly heated, and had become fritted [probably by the action of the glass, as pure quartz would not be fritted at this temperature], was also tinted pale yellow.

A similar experiment was made in which quartz was replaced by oxide of zinc; and the result was the same as in the preceding experiment, except that the mirror-like coating of silver was not so conspicuous.

It was next ascertained that oxide of silver is reduced when heated in oxygen, just as it is when heated in atmospheric air; and in an experiment on this point the same kind of apparatus was used. The quantity of dry oxide of silver operated upon was 4 grammes. A current of oxygen was passed for some time through the tube over the reduced finely-divided silver, kept heated to moderate redness,

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[5] Phil. Trans. 1866. p. 434.
[6] Die metallurgischen Röstprozesse, 1856. p. 121.

whereby a mirror-like sublimate of metallic silver was formed, but less than in the preceding experiments.

Precisely similar experiments, with the substitution of hydrogen and carbonic oxide for oxygen, were made, but no sublimate was produced.

From the foregoing experimental data, Plattner draws the following conclusions:—At a certain moderately high temperature silver is oxidized by gaseous oxygen; at that temperature the oxide of silver formed is volatile; and at a lower temperature the oxide is resolved into silver and oxygen. And on these conclusions he founds a theory in explanation of the loss of silver by volatilization, in the roasting of various argentiferous products. Further, he suggests that the phenomenon of "spitting" is due, not as heretofore believed, to the simple absorption of uncombined oxygen and its subsequent liberation, but to the formation of oxide of silver at a high temperature, and its solution in molten silver, like that of dioxide of copper, Cu^2O [idem], in molten copper; and its resolution at a lower temperature into metallic silver and oxygen.

The experiments of Plattner above described concerning the action of oxygen on finely-divided silver have been repeated with great care in my laboratory, both by Dick and Tookey under my own observation, under exactly the same conditions as he specifies, but not the faintest appearance of sublimation of the metal, and of its deposition on the surface of the tube in the form of a bright annular coating, was observed. That part of the glass, however, upon which the mixture of silver and silica rested was stained yellow. Every precaution was taken to ensure the purity of the oxygen (which was made by heating a mixture of chlorate of potash and oxide of manganese) by passing it over hydrate of potash, and pumice moistened with strong sulphuric acid. Is it possible that the oxygen used by Plattner contained chlorine? It has been shown by Vogel, Poggendorff, and Chevreul that oxygen produced from chlorate of potash contains chlorine:[1] but supposing the oxygen used by Plattner to have been contaminated with chlorine, and chloride of silver to have been produced in consequence, and volatilized, so far as I know there should have been no reduction of such chloride under the circumstances.

Action of various Oxidizing Substances upon Silver.

It is stated by Berthier that when silver in a very fine state of division is heated with protoxide of copper, CuO [idem], minium, Pb^3O^4 [idem], and peroxide of manganese, MnO^2 [idem], it reduces those oxides to their lowest degrees of oxidation, itself being oxidized; and when heated to the melting-point of silver, the greater part of the silver separates in shots or as a button,—a portion, however, of oxide of silver being retained by the other oxides. Silver is also oxidized when melted with sulphate of copper, sulphate of

[1] Chemical Gazette, 1850. 8. p. 17.

lead, nitrate of copper, nitrate of lead, or with several other metallic sulphates and nitrates.[7] We have confirmed the statement of Scheele that molten arsenic acid converts silver into arseniate of silver, with the evolution of arsenious acid.[8]

Action of Water on Silver.

At ordinary temperatures water has no action on silver, whether compact or finely-divided. But, according to Regnault, when steam is passed over pure silver at a white-heat, there is notable disengagement of hydrogen; and the metal on subsequent cooling "spits," owing to the escape of oxygen. Below the temperature of whiteness no hydrogen is evolved.[9] The decomposition in this case was probably the result of simple *dissociation* by heat; for, otherwise, it is difficult to understand why the vapour of water should be decomposed under these conditions, unless we assume that chemical affinity is concerned, and a combination of silver and oxygen is formed. But such an assumption can hardly be reconciled with the fact that oxide of silver is reduced at a much lower temperature. The dissociation of the elements of water, according to H. Sainte-Claire Deville, takes place at about 960° C. or 1000° C.; that is, below the temperature in Regnault's experiments.[1]

The following original observations on this subject by Mr. William Skey, analyst to the Geological Survey of New Zealand, deserve attention: he communicated them to the Wellington Philosophical Society, 29th January, 1876. Pure silver, after immersion for a few hours in distilled water, had its surface so modified that it would not amalgamate immediately afterwards; but this effect was not produced by either rain or spring water. Silver which had been so modified by distilled water, was rendered amalgamable by contact for a short time with rain or spring water, by acetic acid or a solution of ferrous sulphate, or by heating it to 260° C. Silver in dry air did not become unamalgamable. For these, and some other reasons which I have omitted, Skey infers, that in distilled water silver becomes superficially oxidized by the atmospheric oxygen dissolved in the water, and that "the oxides of silver not being reducible or at least easily reducible by mercury, amalgamation is prevented or greatly retarded;" that while in rain or spring water it also becomes superficially oxidized in the same manner, yet the oxide formed is converted into chloride of silver by the chlorides contained in these waters, and that as chloride of silver is readily decomposable by mercury, amalgamation proceeds with rapidity; and, lastly, that perhaps acetic acid acted by dissolving the oxide of silver formed, and ferrous sulphate acted by reducing it to the metallic state. The statement of Skey, that oxide of silver is not reducible or at least not easily reducible by mercury, is entirely opposed to the experience of Malaguti and Durocher. (See p. 11.)

[7] Tr. des Essais, 2. p. 777.
[8] Chemical Essays, 1786. p. 170.
[9] Ann. des Mines, 1837. 3. ser. 11. p. 33.
[1] Société Chimique de Paris. Leçons de Chimie professées en 1864 et 1865, p. 309.

SILVER AND SULPHUR.

SULPHIDE OF SILVER, AgS [Ag^2S].

Silver has a strong affinity for sulphur, and combination takes place even at ordinary temperatures by simple contact of the two elements, as anyone may satisfy himself by rubbing a silver coin with sulphur. The tarnish which silver acquires by exposure to an atmosphere contaminated with animal exhalations containing sulphur is due to the formation of sulphide of silver. Silver decomposes sulphuretted hydrogen at ordinary as well as higher temperatures, with the evolution of hydrogen; though, conversely, hydrogen with the aid of heat reduces sulphide of silver. Combination between silver and sulphur is promoted by heat, and at the temperature of redness is quickly effected. The sulphide may be conveniently prepared by heating a mixture of silver clippings and excess of sulphur in a covered clay crucible, and raising the temperature until the product becomes perfectly liquid. The reaction is accompanied with incandescence. Molten sulphide of silver does not, like molten galena, permeate the substance of the crucible. Thus produced, it is dark grey, feebly metallic in lustre, crystalline, opaque, easily sectile, comparatively soft, somewhat malleable,[2] and has, according to Karsten, a sp. gr. of 6·85;[3] that of native sulphide being 7·196.[4] It crystallizes in the cubic system. It is practically fixed at high temperatures when heated *per se* without access of atmospheric air. It is precipitated in the state of black powder by the addition of sulphuretted hydrogen, or of a soluble alkaline sulphide, to an aqueous solution of a salt of silver. Amorphous, and not crystallized, sulphide of silver is formed when metallic silver and sulphur are heated together with water in a closed tube at 200° C.[5] By whatever method obtained, it is permanent in the atmosphere at ordinary temperatures, whether in the light or in the dark. The fading of photographs, untoned by gold, is due to the transformation of the silver or silver compound constituting the image, into sulphide of silver, which in an extremely thin film is yellowish brown, just like incipient silver tarnish. It is insoluble in water, in aqueous solutions of ammonia or carbonate of ammonia, potash or soda, carbonate of potash or soda, hyposulphite of soda, chloride of potassium or sodium: it is stated that in an aqueous solution of cyanide of potassium it is "nearly insoluble;"[6] but we have found it to dissolve in a very sensible degree in a moderately strong solution of that salt, whether cold or hot, though much more quickly in the latter. The following precise observations on this subject have been made by H. Louis in my laboratory. Of

[2] Berzelius relates that Augustus, king of Poland, caused pieces of native sulphide of silver from the mines of Saxony to be struck into medals. Traité de Chimie, 1846. 2. p. 482.

[3] System der Metallurgie, 5. p. 475.

[4] Brooke and Miller's Mineralogy, 1852. p. 157.

[5] H. Vogel, Jahresber. 1864. p. 142.

[6] Handwörterb. d. Chemie, 1859. 7. p. 969.

pure dry sulphide of silver, made in the *wet* way, 10 grains were digested during an hour and a half in 400 grains of a hot aqueous solution of cyanide of potassium, consisting of 300 grains of water and 100 grains of the cyanide, which was crystallized from an alcoholic solution. After a short time, when the solution, which while cold was colourless, had become hot, it acquired a brownish-yellow tint, and a little sulphuretted hydrogen was evolved. In about an hour the evolution of ammonia was perceived; and after the lapse of an hour and a half the solution was decanted from the undissolved residue, which consisted of sulphide of silver, and amounted to 2·393 grains, so that 7·607 grains of sulphide had been dissolved. On adding water to the decanted solution, until it measured about $\frac{3}{4}$ of a pint, 5·648 grains of sulphide of silver were precipitated. On adding acetic acid to the filtrate a further precipitate of 1·378 grain of sulphide of silver was produced; and on adding nitric acid to the filtrate obtained in this instance, a precipitate of 0·597 grain of cyanide of silver (*i.e.* corresponding to 0·552 grain of sulphide) was formed. There was no proof of the formation of any sulphocyanide of potassium or silver.

Sulphide of silver is insoluble in a solution of the nitrate of peroxide of mercury.[7]

It is acted upon by strong nitric acid, with the formation of nitrate of silver, and the separation of sulphur: the action of diluted nitric acid upon it is given at p. 26 in the sequel. It is stated to be decomposed by "tolerably strong" sulphuric acid, with the formation of sulphate of silver, and the separation of free sulphur;[8] but it is not acted upon when boiled with sulphuric acid diluted with 3 or 4 times its bulk of water. The action of hydrochloric acid on sulphide of silver is stated at p. 42 in the sequel. Sulphide of silver is not acted upon by an aqueous solution of sulphurous acid.[9]

Sulphide of silver was an ingredient of the black substance used in ancient times for inlaying with in what is termed "niello" work.[1] This substance was generally prepared by heating together silver, copper, lead, and sulphur. An account of the mode of making and applying it was written by Theophilus, *alias* Rugerus, priest and monk, early in the eleventh century.[2] An interesting and learned

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[7] Gmelin's Handb. 6. p. 152.

[8] Idem, p. 150.

[9] Guérout, Jahresber. 1872. p. 176.

[1] An interesting historical essay "On Niello," by Mr. Edmund Waterton, was read at the meeting of the Archæological Institute, June 6, 1862, and published in their Transactions.

[2] See the translation of the treatise of Theophilus by Robert Hendrie, London, 1847. p. 237. It is in one volume, which contains the Latin text as well as the English translation. I have found other receipts, some not specifying the use of silver, in old metallurgical treatises and other books.

The following receipt for niello composition is stated to be used in Russia and Persia "for enamelling silver jewels (*argenterie niellée*)."

"Take:—

	oz.	drams.
Silver	0	4
Copper	2	4
Lead	3	4
Flowers of sulphur	12	0
Sal-ammoniac	2	4

Make a paste of the flowers of sulphur and water; put it into a crucible; afterwards melt the metals, and pour them into the crucible which contains the paste; re-cover this vessel, in order that the sulphur may not take fire, then calcine over the fire, until all the superfluous sulphur is driven off; afterwards finely

article entitled "Contributions to the History of Niello-Work," by J. F. L. Hausmann, will be found in Karsten and Von Dechen's Archiv für Minerologie, etc. 1850. 23. pp. 432–443. He gives the following tabular statement of the proportions of the metals used at various times for the preparation of niello-composition, with the addition of sulphur as above described:—

	Silver.	Copper.	Lead.
According to Pliny	75·000	25·000	—
„ Theophilus	66·667	22·222	11·111
„ Biringuccio, „ Benvenuto Cellini, „ Blaise de Vigenère, „ Perez de Vargas	16·667	33·333	50·000
„ Georgi (in Russia)	7·692	38·462	53·846
„ „ Repertory of Patent Inventions, 1827	5·882	35·294	58·824

It will be observed that the proportion of silver is greatest in the oldest niello-composition, in which no lead was used, and least in the most modern, in which lead forms nearly 59% of the weight of the metals.

"*Oxidized*" *silver, so-called.*—This is a misnomer, and the designation should be *brimstonized* silver; but there is a great deal in a name, even in this enlightened age. The surface of objects of embossed silver is rendered dirty lead-grey by the action of sulphur, and is agreeably relieved by deeper tints in the depressed parts. The beautiful and characteristic colour of silver is thus wholly destroyed. The late Mr. George Elkington, by whose taste, energy, and perseverance the art of electroplating was first carried to a practical and really successful issue, gave me the following description of the method which he adopted in the preparation of "oxidized" silver. It consists in keeping the articles immersed in a hot solution of sulphide of potassium until they acquire a sufficiently dark colour, and afterwards brushing or wiping the more prominent parts, which it requires but little experience to do perfectly.

I have met with the following information on this subject:—"There are two distinct shades [of oxidized silver] in use, one produced by chlorine, which has a brownish tint, and the other by sulphur, which has a bluish-black tint. To produce the former, it is only necessary to wash the article with a solution of sal-ammoniac; a much more beautiful tint may however be obtained, by employing a solution composed of equal parts of sulphate of copper and sal-

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pulverize the mass, and make, with the addition of a solution of sal-ammoniac, a paste, which introduce, by means of rubbing, into the parts intended to be enamelled; then clean the article, and place it in a furnace, where it is sufficiently heated to melt the paste which fills the engraved parts and make it adhere to the metal. That done, moisten the article with a solution of sal-ammoniac, and heat it in a muffle to redness; after which you may rub and polish the article when it has become cold, without fear either of altering or detaching the enamel; it remains always of a very fine black colour." (Traité d'Orfévrerie, Bijouterie et Joaillerie, etc. Par Placide Boué. Paris, 1832. 1. p. 284.)

[illegible] by a [illegible] seems [illegible] cannot be [illegible] by, [illegible] is it [illegible] the more rapidly [illegible] coloured [illegible] with the aid of a [illegible] satisfactory [illegible]

[illegible] silver may be easily re- [illegible] obtained by [illegible] and. [illegible] silver may be [illegible] with water in a boil- [illegible] concentrated [illegible] upon [illegible] the [illegible] tarnished by [illegible] exposure [illegible] aqueous [illegible] the tarnish. [illegible] the article [illegible] in the usual manner; [illegible] the salt

[illegible] I [illegible] years, and I [illegible] [illegible] I [illegible] [illegible] of my experience.

"Having [illegible] experiments [illegible] I arrived at the conclusion that a better dip, or *bernish* if you like to call it more cheaply and economically by other means than any I feel it almost a duty, as a grateful attendant at your Lectures on Metals, to inform you of my experience. After trying various substances amongst them chloride of lime dissolved in water, and this, I think, is better than sulphur, I have now for many years used a diluted solution of platinum, with which I am better satisfied than with any previous method. I dissolve platinum clippings in *aqua regia*, taking care to have a surplus of the metal, so that the affinity of the acid at the boiling heat may be thoroughly satisfied. I then filter the solution, after which it is ready for use. A few drops of this solution are mixed with a little water, the strength being regulated according to the darkness of the tint required, and the mixture is applied by means of a soft brush to the parts of an article as it is desired to [illegible] If I wish to hasten the action, I warm the article slightly, but I find this unnecessary, as a film which no heat is applied. The advantages of this method are [illegible] solution is always ready for use, and is very cheap, as a few pennyweights of platinum dissolved will last a number of years; no unpleasant smell is imparted to the work; and any tint from grey to intense black may be produced at will. I will not venture to say anything regarding your strong expressions about the taste of thus discolouring this beautiful metal, further than I concur so far with you as to consider it thoroughly *unsuitable* for articles of domestic use, such as table-plate; but at the same time I must say I think it shows the workmanship of highly artistic work (groups of figures, etc.) to greater advantage, and such work could not be executed with the same perfection in any inferior metal. I know the term 'oxidizing' is a misnomer, but singularly enough it is used both in France and Germany as well as here.

"Your obedient servant,

"P. A. RASMUSSEN, Silversmith.

"26 Harrison Street, W.C.

"Jan. 11, 1870."

[5] Tr. de Chimie, 2. p. 482.

[6] Jahresber. 1857. p. 614.

by washing the article with water. The solution of permanganate of potash loosened the tarnish, so that it could be rubbed off; but the surface of the silver was not left bright by this treatment. Indeed, we find that a solution of the permanganate tarnishes silver, and becomes decolorized, oxide of silver being formed and brown flocks of oxide of manganese precipitated. But in a trial of Böttger's process with borax, the tarnish was not even loosened, much less removed: we have not tried the effect of zinc and a solution of caustic alkali. Silversmiths, I am informed, take off the tarnish from articles of frosted silver by heating them in contact with a mixture of which nitre and carbonate of soda are the chief, if not the sole, ingredients. By such treatment the surface acquires its original dead-white appearance.

Sulphide of silver and metallic silver.—Molten silver dissolves sulphide of silver, but in what proportion has not, to my knowledge, been previously ascertained with certainty. It is said that sulphide of silver and metallic silver melt together in all proportions;[1] but it is certain that the proportions may be such that, on solidification after fusion, separation will occur, and metal will be found at the bottom.

The following experiments on this point have been made in my laboratory. A mixture of 648 grains of silver and 248 grains of sulphide of silver was melted under charcoal in a clay crucible and left to cool therein. The product weighed 896 grains; that is, precisely the same as the original mixture. It consisted of two distinct layers, the upper one resembling sulphide of silver and the lower one silver, of which the fracture was granular and greyish white. The two layers, between which there was some adhesion, were detached as far as practicable from each other, and weighed separately: the weight of the upper layer was 119 grains, and that of the lower 777 grains. The lower or silver layer contained, therefore, rather less than half of the original sulphide, so that its composition might be approximately indicated by the formula $6\,Ag + AgS$ [$12Ag + Ag^2S$]. (By R. Smith.) In the second experiment 260 grains of silver were melted with 100 grains of sulphide, the proportions by weight of the two substances being nearly the same as in the first experiment. The product was similar to that above described. A piece of the lower metallic layer was analysed, and found to be composed as follows:—

	Per cent.
Silver	83·63
Sulphide of silver	16·37
	100·00

In a third experiment silver and sulphide of silver were melted together in the proportions stated in this analysis, when a homogeneous metallic product was obtained without any sulphide on its surface. (The last two experiments were made in my laboratory,

[1] Berzelius, Tr. de Chim. 1846, 2. p. 482. Berthier, Tr. des Essais, 2. p. 781.

in July, 1875, by Edgar Jackson, formerly a student of the Royal School of Mines. The conclusion from the foregoing experiments is that 1·0 parts by weight of nitrous silver are capable of dissolving 1·34 parts of sulphide and of retaining it after solution.

Having occasion to dissolve in nitric acid somewhat diluted several thousand ounces of silver containing some sulphide of silver, I found that a considerable quantity of red-brown powder was left, the nature of which I regret to say I did not properly investigate. It was dissolved by strong nitric acid, though not easily, and seems to have been in some respects similar to the sulphato-sulphide of silver (i.e. a compound of sulphate and sulphide of silver) mentioned by Berzelius,[1] prepared by digesting sulphide of silver with pure nitric acid, and which he describes as a brown-yellow powder, acted upon with difficulty by nitric acid, but resolved by boiling water into sulphate of silver, which dissolves, and sulphide of silver; whereas the brown residue above mentioned was produced in a boiling solution.

The following experiments on this subject have been made in my laboratory. Of sulphide of silver 1·0 grains were digested in hot nitric acid diluted with five times its volume of water so long as any action seemed to take place. There remained undissolved a light brown substance, which was washed on a filter with diluted nitric acid of the same strength as that used for digestion. After this washing, the substance was tested for sulphuric acid, but not a trace was found in it. Another portion was treated with bisulphide of carbon, which dissolved most of it, but left a black substance which proved to be sulphide of silver. Some of the original brown substance was analysed, and found to be composed as follows:—

	Per cent.
Sulphur, free	81·37
Sulphide of silver	18·68
	100·05

Other experiments were made with acid of different degrees of dilution, but in no case was the sulphato-sulphide of silver obtained. The proportions, however, between the free sulphur and the sulphide of silver were found to vary according to the duration of the action of the acid. The conclusion from the foregoing experiments is that, when silver containing sulphide of silver is digested with hot diluted nitric acid, silver is dissolved and a mixture of sulphide of silver and free sulphur left. And further, that by the action of such acid upon sulphide of silver, silver is slowly dissolved as nitrate without conversion of any of the sulphur into sulphuric acid. The particles of sulphide of silver become coated with a deposit of sulphur, which seems greatly to impede, if it does not actually prevent, the action of the nitric acid on the silver of the sulphide. (By Edgar Jackson, July, 1875.)

[1] Tr. de Chimie, 1847, 4. p. 271.

I have found that when silver, impregnated with a little sulphide of silver, is rolled into sheet and used for electrodes in electro-plating after a time black powder of sulphide of silver is left on the surface of the sheet undergoing solution.

Sulphide of silver and other metallic sulphides.—Sulphide of silver seems to combine with sulphide of potassium or sodium, when heated to the melting-point of the product, which appears pretty homogeneous after solidification: it is decomposed by water, the alkaline sulphide dissolving, and the sulphide of silver remaining in the state of fine black powder. Indeed, this method of melting sulphide of silver with an alkaline sulphide soluble in water may be conveniently practised when it is required to reduce compact sulphide of silver to powder. Sulphide of silver seems also to combine with various metallic sulphides in the molten state; and it is, as shown in the preceding volume by the Author on the Metallurgy of Lead, a constituent of various kinds of regulus. These artificial compound argentiferous sulphides have not been thoroughly examined; yet it is probable that such an investigation of them would lead to interesting scientific, if not to valuable practical, results. Sulphide of silver, it should be remembered, is a powerful sulphur-base. Heated with bisulphide of iron, silver is converted into sulphide, with the formation, it is inferred, of protosulphide of iron.

Sulphide of silver and oxygen.—Whether prepared by the *dry* or *wet* way, it undergoes no change at ordinary temperatures when exposed either to dry or moist atmospheric air. As sulphate of silver is a comparatively very stable salt, it might have been reasonably supposed that the reverse would be the case, especially with finely-divided moist sulphide: but it is not so. The following experiment was made by Dick in my laboratory. Sulphide of silver, prepared from nitrate of silver by precipitation with sulphuretted hydrogen, and which after thorough washing had become dry, was exposed to atmospheric air saturated with aqueous vapour from August 8th to September 15th (1855), when it was examined and found to contain not a trace of sulphuric acid, or of any compound of silver capable of being extracted by boiling with water. When heated with free access of atmospheric air at any temperature, even the lowest at which change occurs,* silver is reduced to the metallic state, without the formation of even a trace of sulphate of silver, the sulphur escaping as sulphurous acid. When sulphide of silver is melted in a covered clay crucible, and left to cool therein, a little metallic silver, in the form of a thin crust composed of very small more or less circular patches of radiated structure, may appear on the surface of the solidified button; and I have one specimen presenting numerous minute protuberances of metallic silver on the surface, somewhat suggestive of the structure of small barnacles, so commonly seen on our coasts adherent to rocks and stones. The sulphide of silver,

* Berthier states that, when sulphide of silver is roasted at a low temperature, some sulphate of silver is formed; but that is erroneous. (Tr. des Essais, 2. p. 781.)

under the conditions stated, could only have been imperfectly protected from the action of atmospheric air, and consequently some of the sulphide would necessarily have been reduced; but this does not explain the cause of the particular structure of the silver protuberances just mentioned.

Sulphide of silver and hydrogen.—When heated in a current of hydrogen, sulphide of silver is completely reduced, sulphuretted hydrogen being evolved, and the silver separated in delicate hair-like fibres. The experiment may easily be made in a glass tube, heated by means of a common spirit-lamp, and is well suited for a lecture experiment.

Sulphide of silver and water.—It undergoes no change in water at ordinary temperatures; but when heated, even somewhat below the melting-point of zinc, in a current of steam, according to Bischof, it is completely reduced, the silver being left in hair-like threads exactly resembling native capillary silver. In an experiment by Bischof, sulphuric acid is stated to have been disengaged, which he supposes might be due to the oxygen dissolved in the water used as the source of steam; but on this point nothing conclusive was ascertained.[1] Regnault asserts that sulphide of silver is reduced when heated to redness in steam, with notable evolution of sulphuretted hydrogen.[2]

The following experiment was made by Dick in my laboratory. Sulphide of silver, prepared by precipitation from nitrate of silver by sulphuretted hydrogen, and placed in a little porcelain boat, was heated to strong redness in a porcelain tube, through which a current of steam was passed. Sulphuretted hydrogen was copiously evolved; sulphurous acid was also recognized by its odour; and free sulphur was deposited, just as when disulphide of copper was similarly treated. (See a preceding volume by the Author, containing the Metallurgy of Copper.) When no more sulphuretted hydrogen came over, the boat was gradually withdrawn, and found to contain metallic silver in globules. With the hope of obtaining the reduced silver in the filamentous form, two other similar experiments were made at a temperature below the melting-point of silver, and in one the action was stopped after about 10 minutes. The sulphide had been melted, and free silver seemed to have dissolved in it while it was molten; for when cold its surface was covered with little excrescences of silver, as was disulphide of copper when treated in a similar experiment with steam. It will be noticed that the temperature in the last experiments was much higher than in those of Bischof, so that the reactions would seem to vary with the temperature. In these experiments it is certain that sulphuretted hydrogen, sulphurous acid, and free sulphur escaped from the tube along with the steam in excess. The presence of sulphur is accounted for by the following equation given by Wackenroder, the discoverer of pentathionic acid:[3]—

$$5HO,SO^2+5H^2S=HO,S^5O^5+9HO+5S.$$

$$[5H^2SO^3+5H^2S=H^2S^5O^6+9H^2O+5S.]$$

[1] Lehrb. der chemisch. u. physikalish. Geologie, 1855. 2. p. 2067.

[2] Ann. des Mines, 3. s. 11. p. 49.

[3] The presence of water is stated to

But how is the production of sulphuretted hydrogen along with sulphurous acid to be explained, seeing that oxide of silver could not exist at the temperature at which the experiment was made, and which was *above* the melting-point of silver? These gases are evolved when disulphide of copper is acted upon at a comparatively high temperature by steam; and the explanation usually given is that oxide of copper is formed, which instantly reduces any contiguous unchanged disulphide, with the evolution of sulphurous acid, on the one hand the affinity of sulphur for hydrogen, and on the other that of oxygen for copper, coming into play. In the reduction of sulphide of silver by steam, is it that the oxygen, which becomes free by the combination of an equivalent proportion of the hydrogen of the steam with sulphur, is instantly absorbed by the reduced molten silver, and that the latter, so impregnated with oxygen, exerts a reducing effect on contiguous unchanged sulphide, just as though there had been generated an oxide of silver undecomposable *per se* at the temperature in question?

It was not until long after the preceding paragraph had been in type, that Mr. C. Law, who assisted me in passing the first part of this volume through the press, suggested that possibly the facts observed concerning the action of steam at a high temperature on sulphide of silver or copper might be satisfactorily accounted for by assuming that the sulphur of the sulphide of silver or copper is attacked simultaneously by the oxygen and hydrogen of the steam, with the production of equivalent proportions of sulphurous acid and sulphuretted hydrogen. The question then naturally occurred, whether any reaction would take place at a high temperature between steam and free sulphur. Corenwinder is, so far as I am aware, the only chemist who has experimented on this subject. He found that on passing the vapour of sulphur and steam over red-hot porous substances, such as pumice, or still better pure silica, sulphuretted hydrogen is copiously produced; he makes, however, no mention of sulphurous acid.[4]

In a repetition of this experiment in my laboratory by H. Louis (1876), a mixture of steam and the vapour of sulphur was passed over pumice-stone heated to redness in a glass tube in a gas combustion-furnace, such as is used in organic analysis; when it was observed that sulphurous acid and sulphuretted hydrogen escaped from the tube, together with sulphur in a fine state of division. The gases were recognized by their respective odours; and, in addition, lead-paper was blackened and blue litmus-paper reddened when held in them.

This experiment appears to favour the supposition that the sulphur of the sulphide of silver is attacked simultaneously by the hydrogen and oxygen of the steam; but it should be borne in mind that, in Corenwinder's and the last experiment, a refractory porous or pulverulent substance was used; whilst in those with sulphide of silver and

be essential to the reaction, and has apparently on this account been introduced into the formula given by Wackenroder (Ann. Ch. Pharm. 59. p. 189).

[4] Compt. rend., 1861. 53. p. 140.

steam no such substance was present, a difference of condition which might possibly affect the reaction.

Dr. Fr. A. Moesta has investigated the action of steam on sulphide of silver at different temperatures, and obtained the following results. For this purpose he used glass tubes, which were heated over a gas-flame, or externally by steam. In the latter case, the tube containing the sulphide was placed within another and much larger tube, both tubes being fitted together with corks at each end in the usual manner. Water was put into the space between the two tubes, and kept boiling, a small tube having been inserted in one of the end corks for the escape of steam. By this means the temperature of the sulphide could be kept constantly at 100° C. Reduction takes place most energetically with artificially-made sulphide of silver [whether prepared by precipitation from a silver solution, or by fusion, is not stated], especially when, in order to bring it into a state of finer division, it is intermixed with particles of glass: but nevertheless, the temperature has the greatest influence on the reduction.

In the case of a single tube heated by means of a gas combustion-furnace, it is easy to heat different parts of the tube to different temperatures, so that the influence of temperature may be well observed. At a low red-heat sulphuretted hydrogen is copiously evolved along with the escaping steam. In this way, it is easy, in the course of five or six hours, to separate silver, not only in the "tree-, moss-, and wire-like forms," but also in larger pieces of the weight of a gramme.

When the other apparatus was used, the steam from the inner tube, kept at a temperature of 100° C., was passed into a dilute solution of nitrate of silver, which immediately acquired a brown colour, due to the formation of sulphide of silver. After the experiment had been continued for four or five hours, a considerable quantity of sulphide of silver was formed; and after filtering the solution, evaporating the filtrate to a small volume, and adding thereto chloride of barium, sulphuric acid was shown to be present in sensible quantity. Hence it was inferred that oxidation of the sulphuretted hydrogen had taken place, whilst the whole apparatus was filled with steam. Moesta suggests the following equation as explaining the reaction:—

$$4AgS + 4HO = 4Ag + HO,SO^3 + 3HS.$$

$$[4Ag^2S + 4H^2O = 4Ag + H^2SO^4 + 3H^2S.]$$

Sulphide of Silver and various Metals.[5]—I. *Iron.* It is reduced completely by metallic iron at a red-heat, with the formation of sulphide of iron; but in this case prolonged fusion, frequent stirring, and a slight excess of iron are necessary. If sulphide of silver be combined with disulphide of copper, complete separation of the silver cannot be effected by iron.

Iron has no action upon sulphide of silver, either when triturated with it in the dry state, or in the presence of cold or boiling water. But on the addition of dilute hydrochloric acid, sulphuretted hydrogen

[5] Karsten, System der Metallurgie, 5. p. 476.

is evolved, and metallic silver set free: with zinc and hydrochloric acid the same result is obtained. (By H. Louis, in my laboratory, 1876.)

Malaguti and Durocher assert that sulphide of silver is reduced by iron in a solution of either alum, ferrous sulphate, or cupric sulphate, heated to 100° C.[6] In the last case metallic copper must be set free by the contact of the iron with the cupric sulphate, and the reactions thereby complicated.

II. *Copper.* Sulphide of silver is not completely reduced when heated with copper in excess. The regulus formed contains silver, and the silver separated alloys with the excess of copper.

Sulphide of silver is reduced by contact with copper in water. Precipitated copper was placed in a bottle with sulphide of silver and water; the bottle was corked and then shaken for some time, whereby most of the sulphide of silver became changed into a grey and spongy substance, which acquired a metallic lustre on burnishing, and readily dissolved in warm very dilute nitric acid, which has but little action on sulphide of silver. The conclusion, therefore, is that metallic silver had been separated. (By H. Louis, in my laboratory, 1876.)

But Malaguti and Durocher state that metallic copper has no action on sulphide of silver even in water heated to 100° C., provided the sulphide has been thoroughly freed from acid by washing.[7] There was certainly no acid present in the experiment above reported. On the other hand the same chemists assert that sulphide of silver is much more easily reduced by copper than by iron, in water containing either alum, ferrous sulphate or cupric sulphate, heated to 100° C. On this subject they have recorded the following experiments:—They kept boiling during three hours, in three separate flasks, 100 grammes of water, 0·110 gramme of sulphide of silver (= 0·100 gramme of metallic silver), 10 grammes of ferric oxide, 10 grammes of pieces of sheet copper, and 10 grammes of alum, ferrous sulphate, and cupric sulphate, respectively. They then removed the copper and the saline solutions, added to each of the residues 20 grammes of mercury, along with sufficient water to produce a semi-liquid paste, and kept the whole in agitation during 10 hours. They also subjected the same quantity of sulphide of silver to the action of the same quantities of mercury and pure water during the same period. The results were as follow, the amounts of silver reduced being expressed in hundredths of the amount of silver in the sulphide in each experiment:[8]—

With ferrous sulphate.	With alum.	With cupric sulphate.	With mercury alone.
28·44	83·39	83·39	Traces.

These results are remarkable, and suggest the necessity of further investigation.

Malaguti and Durocher found that when cuprous oxide was used instead of metallic copper, a smaller quantity of silver was reduced

[6] Op. cit. p. 412. [7] Idem. [8] Idem, p. 413.

in the presence either of alum or of sulphate of copper; but the reducing action of cuprous oxide was greater than that of metallic copper in the presence of sulphate of iron.[9]

Experiments precisely similar to those above recorded on the action of copper and cuprous oxide on sulphide of silver, were made by Malaguti and Durocher upon the double sulphide of silver and antimony (pyrargyrite), and the double sulphide of silver and arsenic (proustite), and their results are shown in the following table:[1]—

PERCENTAGE OF THE SILVER EXTRACTED.

	With ferrous sulphate.	With alum.	With cupric sulphate.	Without salts, copper or cuprous oxide.
I. Copper and pyrargyrite	8·8 ...	71·0 ...	71·0 ...	None.
II. Cuprous oxide and proustite.	17·8 ...	22·0 ...	43·0 ...	None.

It is suggested that the comparatively small amount of action in the presence of ferrous sulphate may have been due to the formation of insoluble basic ferric sulphate resulting from atmospheric oxidation of the neutral solution of ferrous sulphate. In No. I., in the presence of alum or cupric sulphate, not more than 71% of the silver was extracted, whereas in the case of sulphide of silver exposed to the same conditions not less than 83·39% was extracted. It is remarkable that proustite should have been so much less acted upon than pyrargyrite.

III. *Lead.* Sulphide of silver is not completely reduced when heated with lead in excess. The regulus formed contains silver, and the silver separated alloys with the excess of lead.

IV. *Mercury.* Sulphide of silver is decomposed when triturated, even at ordinary atmospheric temperatures, with mercury; and when the latter is in excess, silver amalgam is formed. The following equation expresses the reaction which takes place:—

$$AgS + Hg = Ag + HgS.$$
$$[Ag^2S + Hg = 2Ag + HgS.]$$

According to the experiments of Malaguti and Durocher, mercury reduces the sulphide of silver more rapidly than the chloride, whether these compounds of silver be artificially prepared or native.[2] "The reduction of chloride of silver by means of mercury is very slow, especially when water is not present, whereas mere contact of mercury suffices for the reduction of the sulphide." The following details concerning the comparative reducibility of those substances by mercury are interesting and important. Given weights of artificially-prepared sulphide and chloride of silver were mixed respectively with the same weight of ferric oxide, and with sufficient water to form a semi-liquid paste, and then amalgamated under precisely the same conditions, with the same proportion of mercury, when it was found that the chloride of silver reduced was to the sulphide of silver equally reduced : : 1 : 2·74. [The artificial chloride of silver used in this and other experiments by these chemists, was prepared in the wet way and dried at 100° C.[3]] In similar experiments in which clay was substituted for ferric oxide, the reduction of

[9] Op. cit. p. 414. [1] Idem, p. 419. [2] Idem, p. 391. [3] Idem, p. 357.

the chloride was to that of the sulphide : : 1 : 1·76. Hence, in expressing the reducibility of the chloride of silver by 1, there is a difference in favour of the sulphide of silver expressed in one case by 1·74, and in the other by 0·76. The following experiments were made with native sulphide and chloride of silver. Two mixtures, composed each of 10 grammes of ferric oxide, 14 grammes of mercury, and 5 grammes of water, were subjected to amalgamation during 50 hours: one of these mixtures contained 0·1 gramme of native chloride of silver along with its associated matrix, whilst the other contained 0·1 gramme of native sulphide of silver detached from its matrix. The results expressed in hundredths of the argentiferous matter subjected to experiment, are as under:[4]—

Silver obtained by the amalgamation of the native chloride of silver = 10·4.
Do. do. do. sulphide of silver = 38·0.

According to Malaguti and Durocher, the presence of a solution of alum, ferrous sulphate, or cupric sulphate, greatly promotes the reducing action of mercury on sulphide of silver. Under similar conditions, and with an equal weight of the crystals of each of those salts, the relative proportions of silver extracted from a given weight of sulphide of silver by mercury alone, and by mercury with the aid of those salts, were as follow:[5]—

Mercury alone	1·00
Alum	1·34
Ferrous sulphate	1·80
Cupric sulphate	2·83

Mercury also attacks the double sulphide of silver and antimony (pyrargyrite) and the double sulphide of silver and arsenic (proustite), and when in excess silver amalgam is formed;[6] but the action is slower than in the case of sulphide of silver.

It is important to note that there are various native sulphides which contain sulphide of silver in considerable quantity, but from which either no silver or only a small proportion of the total quantity present can be directly extracted by mercury. As examples, the following instances, recorded by Malaguti and Durocher, may be mentioned:[7]—

(*a.*) Blende from Pontpéan, which contained 0·18% of silver, was kept in contact with mercury during four months in a cylindrical bottle placed within a box, fixed on a revolving horizontal axis; but as motion could only be communicated by hand, the bottle could not be kept constantly in agitation.[8] In the course of the period above mentioned, this machine was only in action during 200 hours, the number of rotations per minute being 25. No silver was yielded by this blende to the mercury.

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[4] Malaguti and Durocher, op. cit. pp. 396, 397.
[5] Idem, p. 403. [6] Idem, p. 255.
[7] Idem, pp. 256 et seq.
[8] In this apparatus several bottles could be fixed at a time, and they were arranged in planes perpendicular to the axis of rotation. Op. cit. pp. 256 and 358.

(*b.*) Galena from Freiberg, which contained 3½% of silver, yielded only traces of silver to the mercury after contact with mercury for a month, the machine having been kept in action during 60 hours. This so-called galena is stated to have been a mixture of galena and of the mineral named "Weissgültigerz" by the Germans, which contained 32% of silver (p. 75): this mineral consists essentially of lead, silver, antimony, and sulphur, in variable proportions.

Galena from Sala, in Sweden, which contained 0·87% of silver, was more easily attacked by the mercury. After contact with mercury during 4 months and 200 hours of rotation, the mercury extracted about 18% of the total silver present.

(*c.*) Native sulphide of silver and copper (stromeyerite), which contained 3·8% of silver, was kept in contact with mercury during 15 days and 30 hours of rotation, and the mercury extracted less than 6% of the total quantity of silver present. The specimen of mineral operated upon contained a good deal of matrix.

Malaguti and Durocher experimented upon eleven different specimens of galena, of which ten were from different localities. Their results are presented in the following table :—

Locality.	Silver %.	Silver extracted per 1000 of silver present.
Sala	0·80	183
Freiberg	3·00	0
Huelgoat (large tabular fracture)	0·23	0
Do. (fine-grained)	0·20	0
Beresow (containing selenium)	0·17	0
Ariége (antimonial galena)	0·16	0
Sainte-Marie-aux-Mines	0·05	0
Giromagny	0·05	333
Fahlun	0·036	0
Saxony (compact)	0·033	0
Roure	0·033	0

The details of the treatment of the first two galenas in this table have been previously stated. The other nine were subjected to rotation with mercury during 163 hours, but were in contact with that metal during 960 hours. One only of these nine galenas, that from Giromagny, yielded one-third of its silver to the mercury, while the other eight yielded none. The galena of Sala, which is 16 times richer in silver than that of Giromagny, notwithstanding it was in contact with mercury during 960 hours and the machine was in rotation during 200 of those hours, yielded to the mercury less than ½ of the silver which it contained. Hence, Malaguti and Durocher infer that galenas which are "docile to amalgamation" contain sulphide of silver, of which part at least is in the state of simple mechanical mixture, and that galenas which yield none of their silver to mercury probably contain sulphide of silver in actual combination with the sulphide of lead. It is certain, as has been shown in the volume on the Metallurgy of Lead by the Author, that in some galenas the sulphide of silver is present, partially at least, in such a state of mechanical mixture; for not only have the slimes of some galenas been found to be richer in silver than the mass of the galena, but sulphide of silver has been actually observed to be present in certain galenas.

The same conclusion is drawn by Malaguti and Durocher with respect to the modes of existence of silver in blende. Of seven argentiferous blendes from different localities, which were experimented upon by Malaguti and Durocher, two only yielded to mercury a portion of their silver: that of Transylvania, which contained 0·9% of silver, yielded nearly $\frac{1}{10}$ of its silver, and that of Przibram, which contained 0·06% of silver, yielded about $\frac{1}{4}$ of its silver: the other five blendes yielded none of their silver to mercury, though four of them were much richer in silver than the blende of Przibram; the richest, from Fahlun, containing 0·2% of silver; and the poorest, from Sala, containing each 0·033% of silver.

Argentiferous iron-pyrites from Transylvania, Fahlun, and Radna, and magnetic pyrites from Fahlun, which contained 0·05%, 0·036%, 0·024%, and 0·04% of silver, respectively, yielded none of their silver to mercury; while iron-pyrites and "argentiferous sulphide of copper," both from the same mine at Huelgoat, and containing 0·05% and 4·40% of silver, respectively, yielded 82·7% and 5·8% of their total silver, respectively.

Of six specimens of argentiferous "grey copper ore," only two yielded silver to mercury: one was from Sainte-Marie-aux-Mines, and contained 0·45% of silver, and the other, described as "antimonial grey copper ore," was from Mexico, and contained 0·2% of silver; the former yielded 55·5% of its silver, and the latter the whole of its silver; but in this case the experiment lasted six times as long as the other experiments. In the other four specimens, which yielded no silver to mercury, the richest contained 1·23%, and the poorest 0·093% of silver.

In conclusion, out of 41 specimens (nearly all sulphides) of natural argentiferous mineral substances subjected to direct amalgamation by Malaguti and Durocher, only 15 yielded silver; and if we exclude true silver ores, such as stromeyerite, telluride of silver, and the argentiferous sulphide of Huelgoat, we find that out of 38 specimens one yielded the whole of its silver, and 11 only part of their silver, to mercury. The conditions in the experiments varied much with respect to the percentage of silver, the absolute quantity of silver operated upon, the quantity of mercury, and the duration. Hence, Malaguti and Durocher arrive at the conclusion that in most of the simple or complex sulphides, "the silver takes part (*se trouve engagé*) in multiple combinations from which it is very difficult to extract it by direct amalgamation. In drawing this conclusion, it is assumed that the silver in natural sulphides is not present in the state of chloride, an assumption the truth of which they believe they have established."

Sulphide of silver, heated with potash.—The following experiment has been made in my laboratory by H. Louis (1876):—A mixture of 62 grains of sulphide of silver and 248 grains of potash, that is nearly in the ratio of 2AgS : 9(KO,HO) [Ag^2S : 9KHO], was fused, in a rather dull fire, in a clay crucible. Violent effervescence occurred, due to the escape of water. The product consisted of a button of

silver and slag-like matter. The button weighed 47·9 grains; it was well rounded, very malleable, and white and granular in fracture; it contained no sulphide of silver. The slag-like matter was bright orange-red, resinous in fracture, translucent, and contained much sulphide of silver. It will be seen that 88·7% of the silver was reduced. The reaction is explained by the following equation:—

$$4AgS + 4KO = 4Ag + 3KS + KO,SO^3.$$
$$[4Ag^2S + 4K^2O = 8Ag + 3K^2S + K^2SO^4.]$$

Sulphide of silver, heated with carbonate of soda.—The following experiments have also been made in my laboratory by H. Louis:—A mixture of 62 grains of sulphide of silver and 248 grains (*i.e.* four times the weight) of carbonate of soda was fused, at a moderate heat, for 30 minutes, in a clay crucible: violent effervescence took place. The product consisted of a button of silver and slag-like matter. The button weighed 48·3 grains; it was smooth, rounded, and brittle; its fracture was grey and fibrous; and it contained sulphide of silver. It will be seen that 89·4% of the silver was reduced. The slag-like matter was dark-red, opaque, and dull in fracture; it contained sulphide of sodium, sulphate and a little carbonate of soda, and sulphide of silver. The reaction is similar to that which takes place in the case of sulphide of silver and potash, the carbonic acid producing no effect.

The experiment was repeated with the same quantities, but the fusion was continued for 50 minutes, when effervescence had ceased. The button of silver obtained weighed 51·5 grains, so that 95·4% of the silver was reduced. The slag-like matter was brownish-red, translucent, and resinous in fracture; it contained sulphide of sodium, sulphate and much silicate of soda, and sulphide of silver.

Sulphide of silver, heated with lime.—The following experiment has been made in my laboratory by E. Jackson:—A mixture of 124 grains of sulphide of silver and 56 grains of lime was kept heated in a covered clay crucible at a temperature approaching whiteness during half an hour. When cold, the crucible was broken. The sulphide of silver had collected at the bottom; there was no separation of metallic silver, and no evolution of sulphuretted hydrogen on the addition of hydrochloric acid to the lime. The conclusion, therefore, is that no reaction occurs when sulphide of silver is heated with lime.

Sulphide of silver, heated with chloride of potassium or sodium, and with access of air.—The following experiment has been made in my laboratory by R. Smith:—An intimate mixture of 50 grains of sulphide of silver (=silver 43·55 grains and sulphur 6·45 grains) and 250 grains of rock-salt was kept heated in a shallow cup-shaped clay vessel, called a scorifier, in a muffle during about an hour, at a temperature sufficient to frit but not to melt the salt. The product, when cold, was found to contain several small particles of metallic silver, some of which were surrounded with sulphide of silver, chloride of silver, and sulphate of soda. On the addition of hot water chloride of silver was immediately separated in a curdy state, and on

adding more water a considerable quantity of the same salt was precipitated. The chloride of silver thus formed amounted to 12·91 grains (=silver 9·72 grains and chlorine 3·19 grains), and the sulphuric acid amounted to 3·53 grains (=sulphur 1·412 grain). Now, assuming the silver and the sulphur to be acted upon in equivalent proportions, and the silver to be changed by the salt into chloride and the sulphur into sulphuric acid by the oxygen of the air, the quantity of silver corresponding to 1·412 grain of sulphur, converted into sulphuric acid, is 9·52 grains, whilst the weight of the silver, converted into chloride, was 9·72 grains.

The conclusion from the foregoing data is that part of the sulphide of silver is decomposed by the joint action of chloride of sodium and atmospheric oxygen, with the formation of chloride of silver and sulphate of soda, while another part of the sulphide is resolved into metallic silver and sulphurous acid, as occurs when this sulphide is roasted alone with access of air. The slight excess of silver found in the state of chloride is probably due to the direct action of the chloride of sodium on the metallic silver liberated in the experiment; a reaction to be considered in the sequel.

Sulphide of silver, heated with cyanide of potassium.—This reaction has been examined in my laboratory by R. Smith (1876). In one experiment a mixture of 62 grains of sulphide of silver (containing 54 grains of silver) and 248 grains of cyanide of potassium (not chemically pure, but such as is used in electro-plating) was carefully heated in an open clay crucible, so that the substance within it might be watched. The mixture melted, and the molten mass was poured out: it consisted of a button of metallic silver covered with slag-like matter, which was somewhat crystalline in structure and brownish-red in colour. When this matter was put into water, it for the most part dissolved, forming a clear colourless solution, but there was left an insoluble black powder, which proved to be sulphide of silver. The solution contained both alkaline sulphide and sulphocyanide. The button of silver weighed 45·4 grains: it was white, and finely fibrous in fracture. The weight of the silver not reduced, inclusive of any which may have been lost by volatilization, was 8·6 grains. Hence it appears that, when sulphide of silver is heated with cyanide of potassium in excess, about $\frac{8}{9}$ths of the silver are reduced, the rest remaining in combination with the resulting alkaline sulphide. The colour of the slag-like matter could not be due to sulphocyanide of silver, because this salt is white.

Sulphide of silver, heated with oxide of silver.—The following experiment has been made in my laboratory by R. Smith:—A mixture of 62 grains of sulphide and 116 grains of oxide of silver (*i.e.* in such proportions that the sulphur and oxygen were in the same ratio as in sulphurous acid) was heated in a clay crucible to the melting-point of silver. Metallic silver was separated and poured out, but some shots of the metal adhered to the inner surface of the crucible. The button thus produced weighed 156 grains. Its fracture was bluish-grey, partly granular and partly fibrous, and it was found to contain

some sulphide of silver. The total weight of silver in the original mixture was 162 grains. Sulphurous acid began to be evolved before fusion occurred, and, as the temperature was raised, some of the sulphide appears to have been dissolved by the reduced molten silver. Further, a little oxide of silver may have been directly reduced by heat without acting on the sulphide. In such experiments it is very difficult to obtain absolutely precise results, but the facts above recorded seem clearly to indicate that sulphide and oxide of silver, when heated together, mutually reduce each other, just as in the analogous case of disulphide of copper (cuprous sulphide) and oxide of copper, whether red or black oxide. The reaction in question is as follows :—

$$AgS + 2AgO = 3Ag + SO^2.$$
$$[Ag^2S + 2Ag^2O = 6Ag + SO^2.]$$

Sulphide of silver, heated with oxide of lead.—When a mixture of one equivalent of sulphide of silver and two of oxide of lead (*i.e.* when the sulphur and oxygen are in the same ratio as in sulphurous acid) is heated to redness, complete reduction takes place, according to the following equation :—

$$AgS + 2PbO = AgPb^2 + SO^2.$$
$$[Ag^2S + 2PbO = 2AgPb + SO^2.]$$

When the oxide of lead is in much greater proportion, as in the ratio AgS : 4PbO [Ag^2S : 4PbO], the same reaction occurs without the formation of any sulphate of lead or silver.

Two experiments were made in my laboratory, in clay crucibles, by R. Smith (1876). In the first, the proportions of sulphide of silver and of oxide of lead were in the ratio shown in the above equation. The mixture fused with effervescence, due to the evolution of sulphurous acid; a metallic alloy was produced, which contained sensibly all the silver and lead in the mixture employed.

In the second experiment, a mixture of 62 grains of sulphide of silver and 223 grains of oxide of lead was employed, *i.e.* in the ratio of AgS : 4PbO [Ag^2S : 4PbO]. Sulphurous acid was evolved, as in the first experiment; and the crucible was somewhat corroded, with the formation of slag-like matter, which resembled silicate of lead. The metallic alloy obtained was malleable and comparatively hard; its fracture was fine-grained and bluish-grey. It weighed 152·5 grains; the total quantity of silver and lead, which should have been reduced to form sulphurous acid according to the equation given above, is 157·5 grains: no sensible quantity of sulphate of lead could, therefore, have been formed.

Sulphide of silver, heated with protoxide of copper (cupric oxide).—The following experiment has been made in my laboratory by R. Smith :—A mixture of 62 grains of sulphide of silver and 39·7 grains of protoxide of copper (*i.e.* in such proportions that the sulphur and oxygen were in the same ratio as in sulphurous acid) was heated in a clay crucible. Violent action occurred at the temperature of fusion, and some of the metal was spirted up by the sulphurous acid evolved.

The product was a metallic button, of which the fracture was pale-red, fibrous, and crystalline: it weighed 85·3 grains. If no loss had occurred in the experiment, the button should have weighed 85·7 grains, and have contained 54 grains of silver and 31·7 grains of copper. The following is the reaction which took place:—

$$AgS + 2CuO = AgCu^2 + SO^2.$$
$$[Ag^2S + 2CuO = 2AgCu + SO^2.]$$

Sulphide of silver, heated with sulphate of silver.—The following experiment has been made in my laboratory by R. Smith:—A mixture of 62 grains of sulphide of silver and 78 grains of sulphate of silver (*i.e.* in the ratio of $AgS : AgO,SO^3$ [$Ag^2S : Ag^2SO^4$]) was heated in a clay crucible. The mixture fused with effervescence, due to the evolution of sulphurous acid. The product was metallic silver, with a very white, finely fibrous, fracture. It weighed 107·9 grains. The total quantity of silver present was 108 grains: therefore, practically, the whole of the silver was reduced. The reaction which occurred is shown by the following equation:

$$AgS + AgO,SO^3 = 2Ag + 2SO^2.$$
$$[Ag^2S + Ag^2SO^4 = 4Ag + 2SO^2.]$$

Sulphide of silver, heated with sulphate of soda.—An experiment on this subject has been made in my laboratory by H. Louis (1876):—A mixture of 62 grains of sulphide of silver and 71 grains of sulphate of soda was kept fused in a clay crucible, at a full red-heat, for about 15 minutes, air being excluded; and the crucible and its contents were allowed to cool slowly. A button of sulphide of silver, weighing 61·92 grains, was found at the bottom of the crucible; from which it may be inferred that sulphate of soda has no oxidizing action upon sulphide of silver when heated with it.

Sulphide of silver, heated with nitrate of potash.—The following experiment has been made in my laboratory by R. Smith:—A mixture of 62 grains of sulphide of silver and 186 grains of pure nitrate of potash was heated in a clay crucible, when fusion, attended with effervescence, took place at a low red-heat. The molten contents were poured out, and found to consist of slag-like matter and a button of silver which weighed 52·5 grains. This silver was white, vesicular, and uneven on the surface, from which it may be inferred that while molten it had absorbed oxygen, and evolved it during solidification. The weight of silver in the sulphide operated upon was 54 grains, so that there was a slight loss, due, no doubt, chiefly to particles of metal sticking to the inner surface of the crucible. The slag-like matter was translucent, somewhat crystalline, and of a pale green tint: it dissolved in water, and contained alkaline sulphate, but no silver. From this experiment it may be concluded that when sulphide of silver is heated sufficiently in admixture with an excess of nitrate of potash, the whole of the silver is separated, with the formation of sulphate of potash.

Sulphide of silver and chlorate of potash.—The following experiment

has been made in my laboratory by H. Louis:—A mixture of 62 grains of sulphide of silver and 248 grains (*i.e.* four times the weight) of chlorate of potash was heated in a clay crucible to a temperature considerably below redness. After the lapse of fifteen minutes violent action occurred; five minutes later oxygen began to be evolved with effervescence; ten minutes afterwards, the action having nearly ceased, the contents of the crucible were poured out. The product obtained consisted of reduced, unfused silver, mostly in the state of very fine shots, weighing 17·954 grains; and of slag-like matter, which was moderately fluid when poured out, and became on cooling white, opaque, and vesicular, but blackened rapidly on exposure to light. The percentage composition of the slag-like matter was as follows:—

Chloride of silver	23·82
Chloride of potassium	60·98
Sulphate of potash	14·77
	99·57

A little chlorate of potash probably remained undecomposed. The chief reaction which appears to have occurred may be represented by the following equation:—

$$9AgS+6\,(KO,ClO^5)=3Ag+6AgCl+6(KO,SO^3)+3SO^2+6O.$$
$$[9Ag^2S+12KClO^3=6Ag+12AgCl+6K^2SO^4+3SO^2+6O.]$$

According to this reaction one-third, *i.e.* 18 grains, of the silver should have been reduced; this agrees with the actual quantity found, viz. 17·954 grains.

The experiment was repeated with 62 grains of sulphide of silver and 186 grains (*i.e.* three times the weight) of chlorate of potash, and the mixture was heated to low redness. Violent and almost instantaneous action occurred; the contents of the crucible were poured ten minutes afterwards. Shots of silver and slag-like matter were obtained as before: but the silver only weighed 13·45 grains (*i.e.* nearly one-fourth of the whole silver in the mixture employed).

An experiment was made in my laboratory by E. Jackson to ascertain whether a *solution* of chlorate of potash had any action on sulphide of silver: 20 grains of sulphide of silver were introduced into a concentrated solution of chlorate of potash, and the solution was boiled for several hours on two successive days: no silver was dissolved.

Sulphide of silver and chlorine.—According to H. Rose, it is not acted upon by gaseous chlorine at ordinary temperatures, and is only very slowly decomposed when heated in a current of that gas.[8]

Karsten states that it is attacked by chlorine at ordinary temperatures, and that its conversion into chloride takes place sooner and more completely when it is heated to redness in an atmosphere of chlorine.[9]

[8] Poggendorff's Annalen, 42. p. 540. Quoted in Gmelin's Handb. 6. p. 151.
[9] System der Metallurgie, 5. p. 479.

This action has been very carefully investigated in my laboratory by my friend C. Tookey, formerly assayer at the Hong Kong and Japanese mints; and as the results hitherto published concerning it are discordant and erroneous, it will be necessary here to present a somewhat detailed account of his experiments. The sulphide of silver operated upon was prepared by adding sulphide of ammonium in very slight excess to a solution of chloride of silver in ammonia-water. By such excess the presence of free sulphur in the precipitated sulphide of silver was prevented. The sulphide was perfectly washed by well shaking it at intervals in a stoppered bottle with successive portions of cold water, and then transferring it to a filter: by *dry* assay, very carefully made by R. Smith, it yielded 86·82 per cent. of silver, *i.e.* 0·17 less than the theoretical percentage.

I. Action of dry chlorine.—Of this sulphide of silver 29·70 grains were exposed in a glass tube to a current of dry chlorine at the ordinary temperature (Feb. 12, 1869). Manifest absorption of the gas occurred, considerable heat was developed, and chloride of sulphur was evolved.

Of the same sulphide of silver 30·62 grains were heated in a similar manner in a current of dry chlorine. In this case the action was greatly increased, and the whole of the sulphide was changed into chloride of silver, which ultimately melted. The chloride of sulphur and residual chlorine gas were driven off by heating in a current of carbonic acid. The chloride of silver formed weighed 35·37 grains, the calculated weight being 35·35 grains.

Hence it appears that sulphide of silver is changed by dry chlorine into chloride of silver, and the action is much promoted by heat.

II. Action of chlorine-water.—Of sulphide of silver 20·00 grains were kept during three weeks in a saturated aqueous solution of chlorine in a stoppered bottle, which was shaken at intervals. Chloride of silver was formed, but was not quite white, owing to the intermixture of some unchanged sulphide. The chloride was gently heated in a porcelain crucible until it melted, when some free sulphur was observed to condense on the cool part of the crucible. The fused product was black and weighed 22·74 grains, whereas, if complete conversion of the sulphide into chloride of silver had taken place, it should have weighed 23·14 grains. This product was digested in ammonia-water, whereby chloride of silver was dissolved and some black sulphide of silver was left. Sulphuric acid in considerable proportion was found in the residual supernatant chlorine-water, and it was clear that the greater part of the sulphur of the original sulphide of silver had been oxidized and changed into that acid.

Another similar experiment was made, in which 20 grains of the same sulphide of silver were operated upon, after having been finely ground with water in an agate mortar. The conversion into chloride of silver took place much more rapidly than in the preceding experiment; and in the course of two or three days it seemed to be complete, judging from the colour of the resulting chloride of silver. The quantity of sulphuric acid formed was ascertained, and found to

correspond to 2·589 grains of sulphur; and as the sulphide of silver treated contained 2·58 grains of sulphur, it is clear that the whole of the sulphur of the sulphide had in this case been oxidized and changed into sulphuric acid.

Malaguti and Durocher had long previously obtained the same result; but they kept the bottle, containing the sulphide of silver and chlorine-water, in the dark, whereas in the experiments above recorded light was not excluded.[1]

Sulphide of silver and hydrochloric acid.—The dilute acid has no action on sulphide of silver; but the strong acid, aided by heat, attacks it, with the production of chloride of silver, which in part dissolves, and in part forms a coating over the sulphide, so as to impede or prevent further decomposition.

The following experiments on the action of strong hydrochloric acid on sulphide of silver have been made in my laboratory by E. Jackson. Of sulphide of silver 10 grammes were digested with strong hydrochloric acid, and heat was also applied, when sulphuretted hydrogen was evolved at the commencement. The action was continued during many hours daily for four consecutive days. Most of the chloride of silver formed was in solution in the strong acid; but there was a little residue which consisted of chloride of silver and a very small quantity of sulphide of silver, as proved by the action of strong ammonia-water, which dissolved the former and left the latter. It was found by analysis that of the 10 grammes of original sulphide, 9·76 grammes had been changed into chloride, and only 0·24 gramme remained unchanged, having doubtless been protected by the surrounding chloride of silver.

Sulphide of silver, hydrochloric acid and mercury.—Sonneschmid experimented on the combined action of aqueous hydrochloric acid and mercury on sulphuretted silver ores of Mexico, and found that at ordinary temperatures complete reduction of the sulphide of silver occurred, the whole of the silver amalgamating with the mercury in excess. Chloride of silver is first produced by this action and then decomposed by the mercury, with the formation of calomel. The following is a literal translation of Sonneschmid's own statement on the subject:—"By means of common pure hydrochloric acid and mercury the silver can be extracted from all the finely-ground ores containing it, which are suitable for amalgamation [by the Mexican process]. I have conducted in such wise many experiments on a small scale, which nearly all gave good results. I usually half-filled my little test glass with common but pure and concentrated hydrochloric acid, added thereto 100 parts of finely-ground silver ore and mercury in excess, shook the little glass occasionally, and set it in a window where the sun shone in. Rich silver ores, consisting of red sulphide [*i.e.* pyrargyrite and proustite. See the article on Ores of Silver in the sequel] and sulphide of silver, with iron-pyrites, mixed

[1] Recherches sur l'Association de l'Argent aux Minéraux Métalliques, etc. 1850. p. 247.

with quartzose and calcareous vein-stuff, yield, by such treatment, nearly the whole of their silver in 24 hours, provided the requisite precautions be observed."[2] The following experiment has been made in my laboratory by E. Jackson (July 1875):—To 10 grammes of pure sulphide of silver in powder mercury in excess was added, and then hydrochloric acid sufficient to cover the whole. The action was allowed to go on during 48 hours at about the temperature of 90° C. in the daytime, atmospheric air all the while having free access, and the vessel containing the ingredients having been frequently well shaken. After this treatment the mercury was separated and distilled, when a residue of silver was obtained which corresponded to 9·5 grammes of sulphide of silver.

Sulphate of Silver, AgO,SO^3 [Ag^2SO^4].

It may be easily prepared by adding sulphate of soda to an aqueous solution of nitrate of silver, when it is precipitated in the form of a white crystalline powder; or by heating granulated silver with sulphuric acid, and it is very largely produced in this way in the operation of "parting," *i.e.* separating gold from silver, hereafter to be described. It is desirable that the sulphuric acid should be in excess, in order that the sulphate of silver formed may be kept in solution. The reaction is shown in the following equation:—

$$Ag + 2SO^3 = AgO,SO^3 + SO^2.$$
$$[2Ag + 2SO^3 = Ag^2SO^4 + SO^2.]$$

Hot strong sulphuric acid, such as is usually sold under the name of oil of vitriol, is capable of dissolving so much sulphate of silver as on cooling to become a crystallized mass. In thus dissolving about 1000 ounces of silver at a time, and allowing the solution to cool, I have had interlacing prismatic crystals of the sulphate 2 in. or 3 in. long, or longer; but from what is stated further on, it seems probable that those crystals were an acid sulphate of silver. Vogel states that very finely divided silver dissolves in anhydrous sulphuric acid in the cold without any evolution of sulphurous acid.[3] It is colourless, crystallizes in the prismatic system, and has a sp. gr. of 5·34.[4] It is anhydrous. It dissolves in 88 times its weight of water at 100° C.; and on cooling the greater part of it is deposited in small acicular crystals.[5] According to Rodwell, at 15° C. it dissolves in 31061·8 times its weight of water.[6] A convenient solvent for it is a mixture of sulphuric acid and water

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[2] Beschreibung der spanischen Amalgamation oder Verquickung des in den Erzen verborgenen Silbers, so wie sie bey den Bergwerken in Mexiko gebräuchlich ist, mit ausführlicher Darstellung einer neuen Theorie, nach zwölfjährigen practischen Erfahrungen und auf speciellen Befehl des General-Tribunals der Bergwerke von Neuspanien, beschrieben und erläutert von Friedrich Traugott Sonneschmid. Gotha, 1810. pp. 332-3.

[3] Berzelius, Tr. de Chim. 4. p. 270.

[4] Karsten. Quoted from Gmelin's Handb. 6. p. 154.

[5] Berzelius, Tr. de Chim. 4. p. 270.

[6] Jahresber. 1865. p. 241.

of sp. gr. 1·25. From such a solution copper precipitates the whole of the silver in the form of a bulky, sponge-like, crystalline mass. Silver is also completely separated in the metallic state from its aqueous solution by iron, zinc, tin, and lead.[6] Dioxide of copper (cuprous oxide) also precipitates silver in the metallic state from a solution of sulphate of silver, which silver is mixed with basic sulphate of copper, forming a grey mass, and sulphate of copper is found in the solution: it behaves, in this case, in the same way as an equal weight of a mechanical mixture of metallic copper and protoxide of copper (cupric oxide) would do, provided the weight of the former is the same as that of the copper in the latter.[7]

Sulphate of silver dissolves in nitric acid. It is insoluble in alcohol. It suffers no change by exposure to solar light. It melts at a low red-heat into a yellow liquid, which on solidifying becomes a white crystalline mass. If kept heated for a long time, or if a minute quantity of sulphide of silver be added to it while molten, it acquires a very dark orange colour, and on solidifying becomes a brownish-black crystalline mass. (By H. Louis in my laboratory.) It is completely reduced at a strong red-heat with the evolution of sulphurous acid and oxygen, but it resists a temperature sufficient completely to decompose sulphate of copper or iron (cupric or ferrous sulphate). Hence sulphate of silver may be formed by suitably heating metallic silver in admixture with either of those salts, owing to their evolving, during decomposition, sulphuric acid, partly hydrated and partly anhydrous, which combines with the silver. It is also completely reduced when heated with charcoal to dull redness, with the disengagement of carbonic acid and sulphurous acid in equal volumes.[8] Thus:—

$$AgO,SO^3 + C = Ag + CO^2 + SO^2.$$
$$[Ag^2SO^4 + C = 2Ag + CO^2 + SO^2.]$$

Acid sulphates of silver.—C. Schultz has described the following acid sulphates of silver:—

$$AgO,2SO^3 + HO\ [AgHSO^4].$$

It crystallizes in pale yellowish prisms from a solution of the neutral sulphate in less than 3 times its weight of sulphuric acid.

By adding to such a solution from 8 to 10 parts of sulphuric acid, of the sp. gr. of 1·6 to 1·7, a salt crystallized in prisms and of the following composition is obtained:—

$$AgO,4SO^3 + 5HO.$$
$$[AgH^3(SO^4)^2 + H^2O \text{ or } AgHSO^4 + H^2SO^4 + H^2O.]$$

The same salt is produced in larger crystals by dissolving the neutral sulphate in from 6 to 10 parts of sulphuric acid, and letting

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[6] Fischer, op. cit. p. 113.
[7] H. Rose, Bericht. d. Akadem. d. Wiss. zu Berlin, 1857. p. 311.
[8] Gay-Lussac. Quoted from Gmelin's Handb. 6. p. 154.

the solution become diluted by leaving it exposed to moist air. It begins to melt at 100° C., is perfectly liquid at 150° C., and solidifies on cooling into a largely-foliated crystalline mass, which gradually changes into small flat (*flache*) bright crystals.

When neutral sulphate of silver is dissolved in from only 4 to 6 parts of sulphuric acid, of the sp, gr. 1·75, with the application of heat, pearly foliated crystals separate, which have the following composition :—

$$4AgO,10SO^3 + 10HO.$$
$$[Ag^4H^6(SO^4)^5 + 2H^2O \text{ or } 4(AgHSO^4) + H^2SO^4 + 2H^2O.]$$

In solutions of different degrees of concentration in sulphuric acid yet other salts appear to be formed, which, however, cannot be prepared at will. The neutral sulphate of silver also crystallizes in yellowish rhombic octahedra, on cooling, from its solution in dilute sulphuric acid, or from its solution in concentrated sulphuric acid, if the latter is allowed gradually to absorb water.[2]

Silver and sulphate of sesquioxide of iron (*ferric sulphate*).—According to Wetzlar, silver dissolves slightly, at ordinary temperatures, in an aqueous solution of ferric sulphate, and more readily and in greater proportion when free sulphuric acid is present. He states that the "*red* solution of sulphate of sesquioxide of iron, when heated, dissolves silver and becomes *green*, but, on cooling, deposits it and acquires its original colour." The more free acid the solution of ferric sulphate contains, the more difficult is the precipitation of silver therefrom by ferrous sulphate; and it is only by a great excess of this salt that such precipitation can be effected, and then never completely. This behaviour accords with the fact that there is little or no precipitation of silver from a solution of ferric sulphate which has been heated with the powder of silver, and to which, before cooling, a sufficient quantity of sulphuric acid has been added. Dilute sulphuric acid, when left in contact for any length of time with the powder of silver, does not dissolve a trace of the metal; but if only *one* drop of the solution of ferric sulphate be added, in the course of an hour silver will be found to have dissolved. Wetzlar accounts for this fact as follows:—The ferric sulphate imparts oxygen to the silver, and thereby becomes reduced to ferrous sulphate; but this immediately absorbs oxygen from the air and is brought back to its original state of ferric sulphate; and so these alternate reactions continue, the drop of ferric sulphate solution added, in the case above mentioned, acting as the vehicle for the transference of oxygen from the air to the silver, whereby oxide of silver is produced, which combines with the sulphuric acid to form sulphate of silver.[1]

According to A. Vogel, silver dissolves easily and completely in a boiling solution of ferric sulphate, though it be made as neutral as possible by the addition of hydrated sesquioxide of

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[2] Jahresber. 1868. p. 154.

[1] Wetzlar, Schweigger's Jahrbuch der Chem. u. Phys. 1828. 23. p. 94.

iron. In this reaction the silver is oxidized, with an equivalent reduction of sesquioxide to protoxide of iron, and sulphate of silver is formed. Silver is not in the least degree acted upon by a boiling aqueous solution of pure ferrous sulphate; but if even a slight quantity of sesquioxide of iron [in the state of ferric sulphate?] be present in the solution, some silver will dissolve in it on boiling, of which part will be thrown down in the metallic state on cooling, owing to the presence of so large a quantity of protoxide of iron in the state of ferrous sulphate.[2]

It is stated on the authority of Wöhler, that a hot solution of ferrous sulphate dissolves metallic silver, which, on the subsequent cooling of the solution, is precipitated.[3] I have boiled precipitated silver for a considerable time in a moderately strong aqueous solution of pure ferrous sulphate, with free access of air, and found that not a trace of silver was dissolved: the solution became turbid and deposited a small quantity of light-brown matter. I then added some sulphuric acid to this solution, and boiled it again until it was rendered nearly bright, but found no trace of silver in the solution.

Stripping liquor.—There is an old receipt, still in use, for dissolving silver off old articles of silver-plated copper: it is to boil the plated metal in a menstruum composed of 3 lbs. of oil of vitrol, 1 lb. of water, and 1½ ounce of nitre, until the silver is removed. Common salt is added to the solution thus obtained, whereby chloride of silver is thrown down, from which the metal is recovered.[4] Keir was the first to discover this solvent of silver, which he prepared by dissolving 1 part by weight of nitre in 8 or 10 of strong sulphuric acid. This liquid should be used at a temperature of from 38° C. to 93° C. (100° F. to 200° F.); it dissolves about ⅛ or ⅙ of its weight of silver much more easily than sulphuric acid alone would do; undiluted, it partially dissolves tin and mercury, but hardly touches copper, lead, or iron; if diluted with water, its power of dissolving silver is much lessened, and it then attacks copper with ease.[5]

Keir's own instructions for applying this solvent are as follow:—"Nothing more is required than to put the pieces of metal into an earthen glazed pan; to pour upon them some of the acid liquor, which may be in the proportions of 8 or 10 lbs. of oil of vitriol to 1 lb. of nitre; to stir them about, that the surfaces may be exposed to fresh liquor, and to assist the action by a gentle heat from 100° to 200° Fahr. When the liquor is nearly saturated, the silver is to be precipitated from it by common salt, which forms a luna cornea, easily reducible by melting it in a crucible with a sufficient quantity of potash; and lastly, by refining the melted silver, if necessary, with a little nitre thrown upon it. In this manner the silver will be obtained sufficiently pure, and the copper will remain unchanged.

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[2] Storer's Dictionary of Solubilities, p. 558; where the following authority is referred to:—A. Vogel, Journ. für prakt. Chem. 1840. 20. p. 365.

[3] Malaguti and Durocher, op. cit. p. 252.

[4] Richardson's Chemical Principles of the Metallic Arts. Birmingham, 1790. p. 112.

[5] Phil. Trans. 1790. 80. p. 367; and Aikin's Dictionary, 1807. 2. p. 316.

Otherwise, the silver may be precipitated in its metallic state, by adding to the solution of silver a few of the pieces of copper, and a sufficient quantity of water to enable the liquor to act upon the copper."[6]

Sulphite of Silver, AgO,SO^2 [Ag^2SO^3].

The statements in chemical treatises concerning this salt are far from concordant. It is colourless, and is deposited in small white brilliant crystals by the addition of an alkaline sulphite, or of sulphurous acid, to the aqueous solution of a salt of silver. It suffers no change by exposure to sunlight.[7]

According to Geitner, when sulphite of silver is heated to 200° C. with water, it is resolved into crystallized metallic silver and sulphate of silver;[8] and when metallic silver is heated in a closed tube to 200° C., in an aqueous solution of sulphurous acid, microscopic crystals of argentic sulphide, resembling the native sulphide, are produced: similar crystals are also formed with nitrate of silver under the same conditions; but chloride of silver, in diluted acid, only shrinks up and darkens in colour, without undergoing further change. (See also the article on Nitrate of Silver in the sequel.)

We are indebted to Stas for the following observations on this salt, which are particularly interesting with regard to the action of solar light. When a current of sulphurous acid is passed into an aqueous solution of nitrate or sulphate of silver, white sulphite of silver is precipitated, and the liquid remains colourless. A solution of sulphurous acid, freshly prepared by passing the gas through water previously boiled and kept from exposure to sunlight, acts in the same manner as the gas itself. Sulphite of silver, when protected from the action of light, undergoes no change at the ordinary temperature; but under the influence of light and an excess of sulphurous acid, it is changed into a mixture of sulphate of silver and metallic silver. A current of sulphurous acid, and a freshly-made saturated aqueous solution of this gas, do not produce any precipitate of sulphite of silver in a solution of nitrate, or in one of sulphate of silver sufficiently acidulated with sulphuric or nitric acid. In perfect darkness, sulphurous acid may even be kept for a long time at a temperature approaching 100° C., in contact with nitrate or sulphate of silver dissolved in dilute sulphuric acid, without causing the least colouring in the liquid or any precipitation. On the other hand, a solution of sulphurous acid in water, boiled or not boiled, after having been left for some time even in diffuse light, produces a grey precipitate in a solution of nitrate or sulphate of silver; and after a few moments the liquid, in which the precipitate has been formed, becomes yellow, brown, then black, and at lasts deposits sulphide of silver. Stas further says he has seen such a solution of altered sulphurous acid throw down metallic silver in the dark from a solution of nitrate or

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[6] Phil. Trans. 1790. 80. p. 368.
[7] Berzelius, Tr. de Chim. 4. p. 271.
[8] Jahresber. 1864. p. 142.

sulphate of silver in dilute sulphuric acid, and even in dilute nitric acid.[9] O. Loew reports that he kept dilute solutions of sulphurous acid, in closed glass tubes, during a whole summer exposed to the sun's rays. During two months they remained clear, but then became turbid, and the more so the longer they were exposed. Sulphuric acid was formed, and sulphur separated. He adds that, under exactly the same conditions, solutions of salts of sulphurous acid were not affected by light; but he does not specially mention sulphite of silver.[1] When solutions of salts of silver are boiled with an excess of alkaline sulphite, silver of great purity is precipitated in the form of white powder; but never less than half of the silver resists reduction and remains in solution. However, on adding to the boiling liquid ammonia in excess, and any soluble salt of copper whatever, the whole of the silver is instantly precipitated. Under the influence of ammonia, the soluble sulphites with the aid of heat reduce salts of protoxide of copper to salts of dioxide; and ammoniacal salts of the latter immediately reduce all the ammoniacal compounds of silver, with precipitation of pure silver.[2]

At a temperature bordering on incipient redness, sulphite of silver is resolved into sulphate of silver and metallic silver.[3] It combines with neutral sulphite of potash or soda, forming double sulphites soluble in water; and these salts have a special point of interest with respect to electro-metallurgy. The late Mr. John Stephen Woolrich, whom I knew well, obtained a patent for the application of the magneto-electric current, developed by a machine of particular construction contrived by himself, to the "coating with metal the surface of articles formed of metal or metallic alloys."[4] The solution, which he employed for plating with silver, was prepared by adding sulphite of potash to an aqueous solution of nitrate of silver, and redissolving the precipitated sulphite of silver in excess of the precipitant;[5] or, as he informed me, by dissolving oxide of silver in an alkaline sulphite containing an excess of alkali. I have such a solution made by himself, from which metallic silver has been deposited in the form of a coating having metallic lustre on the internal

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[9] Nouvelles Recherches, etc. Op. antea cit.

[1] Jahresber. 1873. p. 164.

[2] Stas, op. cit.

[3] Gmelin's Handb. 6. p. 153.

[4] Abridgments of Specifications relating to Electricity and Magnetism, their Generation and Applications, 1859. p. 71. The patent is dated A.D. 1842, Aug. 1, No. 9431.

[5] The specification of the patent contains the following directions for the preparation of the "silvering liquor:"—To make the sulphite of potash solution, 28 lbs. of pearlash are to be boiled in 30 lbs. of water until dissolved; the solution is to be filtered when cold, and 14 lbs. of distilled water added to the filtrate: sulphurous acid gas is then passed through the filtrate until the latter is saturated, care being taken that the sulphurous acid is not added in excess; and the solution is again filtered. To make the nitrate of silver solution, 12 oz. of crystallized nitrate of silver are dissolved in 3 lbs. of distilled water. To this solution the sulphite of potash solution is to be added so long as a whitish-coloured precipitate is produced. The precipitate is to be allowed to subside; the supernatant liquid poured off; and the precipitate washed with distilled water and afterwards dissolved in a further quantity of the sulphite of potash solution, about one-sixth more of the solution being added than is required to dissolve the precipitate. After filtering the solution thereby produced, it is ready for use.

surface of the bottle in which it was contained: he informed me (in 1845) that such deposition of silver takes place on a surface of glass or earthenware, but not upon wood; and that it is independent of the action of light. I have often seen electro-plating with silver thus carried on by Mr. Thomas Prime, of Northwood Street, Birmingham; and in 1845 I conducted Mr. and Mrs. Faraday to Mr. Prime's works, where for the first time that great philosopher saw his discovery of the magneto-electric current applied to the electro-deposition of silver. I shall never forget the sparkling delight which he manifested on seeing this result of his purely scientific labours rendered subservient to a beautiful art and to the advantage of others. But for sulphite of silver, Woolrich's invention would have been of no avail; for Elkington had previously obtained patents for the electro-deposition of silver by means of the voltaic current, and for the use in connection therewith not only of the alkaline cyanides as solvents of silver, but of about 430 additional salts![6] Luckily for Woolrich, the double salts of sulphite of silver and alkaline sulphites were not amongst the number.

Hyposulphite[7] or Dithionite of Silver, AgO,S^2O^2 [$Ag^2S^2O^3$].

The process prescribed for its preparation is as follows:[8]—An aqueous solution of nitrate of silver of moderate strength is added to an excess of a pretty strong aqueous solution of hyposulphite of potash, when a grey substance is precipitated consisting of a mixture of hyposulphite and sulphide of silver. The precipitate is washed with cold water, and afterwards treated by an aqueous solution of ammonia, which dissolves out the hyposulphite of silver without acting on the sulphide; the ammoniacal solution is exactly neutralized by nitric acid, whereby the salt is precipitated, which must be dried as quickly as possible by pressure between bibulous paper. Thus made, it is described as a snow-white powder, having a sweet savour, and being sparingly soluble in water. It is easily decomposed in the manner shown by the equation—

$$AgO,S^2O^2 = AgS + SO^3 \quad [Ag^2S^2O^3 = Ag^2S + SO^3].$$

It forms various double salts, only two of which here need attention,

[6] A.D. 1842, June 1, No. 9374. The patent was granted to Henry Beaumont Leeson, and became the property of Elkington, who had secured Dr. Leeson's professional services for the purpose. A Memorandum of Alteration was enrolled by the patentee, dated March 25, 1843, i.e. after the date of Woolrich's patent, in which the terms sulphate of silver, sulphate of silver and soda, sulphate of silver and potassa were altered into sulphite of silver, sulphite of silver and soda, and sulphite of silver and potassa. In what other country would such an alteration have been allowed? Elkington subsequently purchased Woolrich's patent. Such a patent as that granted to Dr. Leeson would not be granted since the Patent Law Amendment Act, 1852.

[7] It has been proposed to substitute the terms *thiosulphate* or *sulphosulphate* for hyposulphite, to designate the salts of the acid commonly known as hyposulphurous acid, HO,S^2O^2 [$H^2S^2O^3$]: in order that the term hyposulphite may be applied to the salts of a new acid, HO,SO [H^2SO^2], discovered by Schützenberger.

[8] Gmelin's Handbook, 6. p. 152. Berzelius, Tr. de Chim. 4. p. 272. Handwörterb. der Chemie, 7. p. 626.

namely, the hyposulphites of silver and soda. Their formulæ are given as under :—

I.—$AgO,S^2O^2+2(NaO,S^2O^2)+2HO$ [$Ag^2S^2O^3+2(Na^2S^2O^3)+2H^2O$].
II.—AgO,S^2O^2+NaO,S^2O^2+HO [$Ag^2S^2O^3+Na^2S^2O^3+H^2O$].

The first is obtained by continuing very gradually to add an aqueous solution of nitrate of silver to an aqueous solution of hyposulphite of soda until a permanent precipitate begins to appear; alcohol is then poured in, whereby the salt is thrown down in shining scales, which must be washed with alcohol, and dried in vacuo over sulphuric acid. If, instead of alcohol, the addition of the solution of silver is continued, the second salt is precipitated in white flocks, which soon become crystalline. The aqueous solutions of both salts have a remarkably sweet savour. Both salts dissolve in excess of the solution of hyposulphite of soda, as also in ammonia. Oxide of silver, and all the insoluble silver salts, even the chloride, bromide, and iodide, dissolve completely in a cold, pretty strong aqueous solution of hyposulphite of soda. But this is not a case of simple solution, as decomposition occurs with the formation of double hyposulphite of silver and soda. When oxide of silver is dissolved in this menstruum, soda is set free. It is only an aqueous solution of the first salt in water containing excess of hyposulphite of soda that concerns the metallurgist as well as the photographer. This solution acquires a dark brown colour on keeping, owing to the formation of sulphide of silver. On boiling, it immediately becomes dark brown ; and if to the boiling solution excess of hydrochloric or dilute sulphuric acid is added, the whole of the silver is quickly precipitated as sulphide in admixture with free sulphur, while sulphurous acid is at the same time copiously disengaged. The precipitate may be rapidly and completely washed with hot water. This process may conveniently be adopted for the recovery of silver from old photographic hyposulphite solutions. By melting the sulphide of silver with carbonate of soda and nitre the silver is wholly reduced. The following equation explains the previous reaction :—

$2(AgO,S^2O^2+NaO,S^2O^2)+2HCl = 2AgS + S+5SO^2 + 2NaCl + 2HO.$
[$2(Ag^2S^2O^3+Na^2S^2O^3)+4HCl = 2Ag^2S+S+5SO^2+4NaCl+2H^2O.$]

The silver is wholly precipitated from its solution in hyposulphite of soda by sulphide of sodium; and of this fact Patera has availed himself in a process to be hereafter described.

In order to ascertain whether the precipitate, resulting from the addition either of sulphuric or hydrochloric acid to a solution of chloride of silver in an aqueous solution of hyposulphite of silver, contained any chloride of silver, the following experiments were made in my laboratory by Dick. An aqueous solution of hyposulphite of soda was saturated cold with chloride of silver, and filtered from the excess of the latter. The filtrate was acidified with dilute sulphuric acid and boiled. The precipitate formed was thoroughly washed with water, and digested with nitric acid. The insoluble residue of sulphur

was thoroughly washed with water, dried, and heated; but there was no residue containing chloride of silver.

A similar solution of chloride of silver and hyposulphite of soda was divided into two portions, which were boiled, and, while boiling, hydrochloric acid was poured into one, and dilute sulphuric acid into the other. The precipitates were examined, just as in the last experiment. That produced by hydrochloric acid contained but a minute trace of chloride of silver, while that produced by sulphuric acid contained chloride of silver in considerable quantity. This discrepancy, it was thought, might be due to the fact, that chloride of silver is soluble in a notable degree in a solution of chloride of sodium, and not in one of sulphate of soda.

Chloride of silver was dissolved in an aqueous solution of hyposulphite of soda containing an *excess* of the latter, and was treated exactly as in the last experiment. No chloride of silver was found in the precipitate, obtained either with sulphuric or hydrochloric acid. In all these experiments the precipitates were nearly white, with a greyish tint, for an instant after their formation by the addition of acid; but they rapidly darkened, especially in the boiling solutions; and in all, sulphurous acid was evolved in large quantity. Hence, when there is excess of hyposulphite of soda, the precipitated sulphide of silver is free from chloride of silver.

SILVER AND SELENIUM.

What is known on this subject is chiefly due to Berzelius, and is as follows:—"It is easy to combine silver with selenium. Silver is blackened by the vapour of selenium, by selenious acid, and by seleniuretted hydrogen. Combination may quite as easily be effected in the wet way, by precipitation from a salt of silver by seleniuretted hydrogen, as in the dry way, by melting selenium with silver. The selenide formed in the wet way melts readily into a globule of silver-whiteness (?), which is capable of being flattened a little, and which cannot be entirely freed from selenium, either by roasting, or by fusion with borax, alkali, or iron; the latter dissolves in it, and forms a granular, deep-coloured, yellowish-grey compound. When selenide of silver, produced by precipitation, is melted with selenium, it takes up a certain quantity of it, which it retains even at a red-heat. On melting, its surface becomes mirror-like; after cooling, it is grey and soft. The portion of selenium so added may be driven off by roasting. Selenide of silver is a very strong selenium-base; that which is obtained by precipitation consists of 73·16 parts of silver and 26·84 of selenium, or of one atom of each of the two elements, and its formula, therefore, is AgSe [Ag^2Se]. In the selenide, which is saturated with selenium by fusion, the silver is united to double the quantity of selenium, or 57·68 parts of silver are combined with 42·32 of selenium, which corresponds to the formula $AgSe^2$ [AgSe]."[1]

A mixture of 43·2 grains of precipitated silver and 15·9 grains of

[1] Traité de Chimie, 1846. 2. p. 484.

selenium, *i.e.* in the ratio of equivalent to equivalent, was heated in a hard-glass tube over a Bunsen air-gas flame. Combination occurred, but without very decided incandescence. As the temperature did not suffice perfectly to melt the product, the tube was heated over a blow-pipe air-gas flame, when complete fusion occurred. The product was dark bluish-grey, sub-metallic in lustre, much harder and more brittle than sulphide of silver, and much less sectile: it weighed 57·2 grains, thus showing a loss of 1·9 grain, which, however, was mainly due to the adhesion of particles of the product to the tube. Only a minute quantity of selenium sublimed. I perceived a strong and decided odour of sulphurous acid at the mouth of the tube, so that the selenium must have contained sulphur, notwithstanding it came originally from the late Professor Mitscherlich.

Selenite of Silver, AgO,SeO^2 [Ag^2SeO^3].

"It is obtained by mixing nitrate of silver with selenious acid, when it is precipitated in the form of white powder. It dissolves in small quantity in boiling water; but it is thrown down when cold water is added to the solution. The solution is not rendered turbid by dilution with boiling water; and when it is allowed to cool gradually, the salt crystallizes in white needles. It is not blackened by light, melts at nearly the same temperature as the chloride of silver, and becomes on cooling an opaque, white, brittle mass, which has a crystalline fracture. When this salt is strongly heated, oxygen gas is evolved and selenious acid volatilized, and the selenite becomes covered with a film of metallic silver." [2]

Selenate of Silver, AgO,SeO^3 [Ag^2SeO^4].

It has much analogy with the sulphate of silver in respect of colour, crystalline form, and solubility. It may be obtained by dissolving silver in selenic acid.[3]

Selenium in Commercial Silver.

Debray announces that he has found selenium to be almost constantly present in refined silver, and attributes it to the contamination of the sulphuric acid now used in the process of parting, to be described in the sequel; in which process auriferous alloys of silver are boiled with sulphuric acid in cast-iron vessels, when the silver alone dissolves. From the sulphate of silver thus obtained, the silver is separated in the metallic state by copper or iron. Sulphuric acid is chiefly made from iron-pyrites, which, if Debray's announcement be correct, must generally contain selenium; and, according to him, some varieties contain so much as to yield sulphuric acid contaminated with selenious acid in notable quantity. When, in the process of parting, seleniferous sulphuric acid has been used, and copper for separating the silver, nearly the whole of the selenium is precipitated along with

[2] Berzelius, op. cit. 4. p. 292.
[3] Idem; and Mitscherlich, Handwörterb. d. Chemie, 1859. 7. p. 826.

the silver, which, after fusion, will consequently be seleniferous. When such silver is melted with *dry* copper, *i.e.* copper which contains cuprous oxide in notable quantity, lively effervescence occurs, owing to the reaction between the oxide and the selenium, whereby selenious acid is formed and volatilized. According to Debray, the presence of sensibly less than $\frac{1}{1000}$th of selenium is sufficient to "poison" (*empoisonner*) silver. Selenium may be detected in silver by dissolving the metal in dilute nitric acid (of 1·075 to 1·116 sp. gr.), when small, crystalline, greyish plates of a metallic aspect, and consisting of selenide of silver, will be deposited; which plates are only a little acted upon by dilute nitric acid, but dissolve easily in the concentrated acid. Silver may be easily freed from selenium by melting it in an oxidizing atmosphere, or in admixture with nitrate of soda or potash.[4]

The following experiments have been made in my laboratory by H. Louis (1876):—

(1.) A mixture of 25·7 grains of pure silver and 1·0 grain of selenide of silver (containing about 26·77% of selenium and 73·23% of silver) was introduced into a small clay crucible, in the upper part of which a plug of charcoal was afterwards fitted, and a cover then placed over the whole. The crucible was heated to bright redness for ten minutes, and afterwards gradually allowed to cool. When cold, the crucible was opened and found to contain a well-melted button, which weighed 26·67 grains, showing a loss of 0·03 grain, and, from the composition of the mixture employed, must have contained about 1·0% of selenium. The button was well rounded, dull and crystalline on the surface, which presented skeleton octahedra; its fracture was grey, irregularly fibrous or hackly, and resembled that of silver containing a little sulphide. The metal was moderately malleable. A portion of the button was slowly dissolved in warm nitric acid of sp. gr. 1·1: only a trace of black residue was left, which was found to be perfectly amorphous even when highly magnified, and disappeared on being heated over an air-gas flame; it was probably selenium. From the solution the silver was precipitated as chloride, and filtered off. The filtrate gave no precipitate on the addition of chloride of barium; but with sulphurous acid a red precipitate was obtained, whence it was inferred that the selenium was present in the solution in the state of selenious acid.

(2.) A mixture of 26·6 grains of pure silver and 0·1 grain of the selenide of silver, containing about 26·77% of selenium, was treated in exactly the same way as the previous mixture. The button produced weighed 26·67 grains, showing a loss of 0·03 grain, and, from the composition of the mixture employed, must have contained about 0·1% of selenium. The button resembled that obtained in the last experiment, except that the crystalline structure was not so distinct; its fracture was white, similar to that of pure silver: the metal was very malleable. A portion of the button was treated in

[4] Compt. rend. 1876. 82. p. 1156.

precisely the same way as in the last experiment; and similar results were obtained.

It will be seen that these results do not agree with the statement of Debray above recorded, concerning the action of dilute nitric acid on seleniferous silver.

SILVER AND TELLURIUM.

I have not met with any record of experiments on the direct combination of these elements with the aid of heat; but, according to Parkmann, a precipitate of telluride of silver is formed when a piece of tellurium is immersed in a solution of a salt of silver.[5] A native telluride of silver is known, which has the formula AgTe [Ag^2Te]; it is designated hessite, and will be further noticed in the article in the sequel on the Ores of Silver. It is easily fusible. The silver may be separated from it by the following process:—mixing the triturated telluride with nitre, and projecting the mixture in successive portions into a crucible containing molten potash. After the whole has been thus added, and effervescence has ceased, the temperature is to be raised sufficiently to melt the mass, after which the silver will be found melted at the bottom of the crucible.[6]

Malaguti and Durocher state that they found that mercury, by long contact and occasional agitation with Siberian telluride of silver, extracted 88·4% of its silver, 76·0% after preliminary treatment of the telluride by an aqueous solution of cupric chloride, and 84·0% after the same treatment with the addition of chloride of sodium.[7] But elsewhere (p. 263) they state that only 76·0% was extracted by the direct action of mercury.

TELLURITE OF SILVER, AgO,TeO^2 [Ag^2TeO^3].

When a solution of neutral tellurite of potash or soda, *i.e.* of the formula RO,TeO^2 [R^2TeO^3], is added to a neutral solution of nitrate of silver, tellurite of silver is precipitated as a bulky yellowish-white precipitate which dissolves in ammonia-water; and when this solution is evaporated, a grey-blue basic salt is deposited.[8]

TELLURATES OF SILVER.

For our knowledge of this subject we are indebted almost wholly to Berzelius, who described the five following salts.

Tellurate of silver, of the formula AgO,TeO^3 [Ag^2TeO^4], is precipitated as a deep-yellow powder when a solution of pure tellurate of potash (*i.e.* of the formula KO,TeO^3 [K^2TeO^4]) is added to a perfectly neutral solution of nitrate of silver. By water it is resolved into an insoluble basic salt, and an acid salt which remains in solution along with a portion of undecomposed salt. Hence it is that this tellurate is produced only with solutions of a certain degree of concentration. When the salt is washed on a filter, it becomes deeper

[5] Jahresber. 1861. p. 128.
[6] Berzelius, Jahres-Ber. 1835. p. 182.
[7] Op. cit. p. 430.
[8] Berzelius, op. cit. p. 293.

and deeper in colour; and if the washing is effected with boiling water, there remains at last a basic salt of the colour of liver, which has the formula $3AgO,2TeO^3$ [$Ag^6Te^2O^6$]. Tellurate of silver dissolves in ammonia-water, forming a colourless solution; and when a mixture of this solution and an ammoniacal solution of nitrate of silver is evaporated, there is produced a black-brown precipitate of basic tellurate of the formula $3AgO,TeO^3$ [Ag^6TeO^6]. All these tellurates are anhydrous.

By the addition of alkaline bi- and quadrotellurates to a concentrated solution of silver, copious flocculent precipitates of a pure red-yellow colour of bi- and quadrotellurates of silver are respectively produced. If these solutions are mixed after having been much diluted, a precipitate is formed, which at first is yellow-red, and immediately afterwards becomes black-brown, owing to its transformation into a basic salt by the action of the water.[1]

Sulpho-tellurite of Silver, $3AgS,TeS^2$ [Ag^6TeS^5].

By adding a solution of sulpho-tellurite of potassium, of the formula $3KS,TeS^2$ [K^6TeS^5] (which is prepared by passing sulphuretted hydrogen through a solution of tellurate of potash), to a neutral solution of nitrate of silver, a copious black precipitate of this salt is formed, which acquires a metallic lustre by burnishing. When heated in a close vessel, sulphur is volatilized, and there remains a fused metallic button apparently of telluride of silver, which has a leaden-grey colour, is as ductile as lead, may be flattened out without cracking at the edges, and is not changed when melted in contact with the air.[2]

Chloride of Silver and Tellurium.

According to Berzelius, when tellurium and chloride of silver are melted together they combine, forming a white hard mass, which is metallic in lustre and crystalline in fracture; but he did not ascertain its composition.[3]

SILVER AND CHLORINE.

Dichloride of Silver, Ag^2Cl [idem].

This salt is produced by the action of hydrochloric acid on argentous oxide, or by the addition of the same acid or chloride of sodium to a solution of a salt of argentous oxide, such as the citrate, when it is precipitated as a brown curdy substance, which on drying at a gentle heat becomes black: and, on the other hand, it is said to be formed by the action of chloride of ammonium on metallic silver, provided there be access of air (see p. 65 in the sequel). It is resolved at the melting-point of chloride of silver (argentic chloride) into this chloride and finely-divided metallic silver. It is decomposed

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[1] Berzelius, Traité de Chimie, 1847. 4. p. 292.

[2] Berzelius, op. cit. p. 297.

[3] Gmelin's Handbook, 6. p. 193.

in like manner by caustic ammonia, or by a concentrated solution of chloride of ammonium, the resulting chloride of silver dissolving and metallic silver remaining undissolved. According to Wetzlar, when a solution of cupric or ferric chloride is poured upon silver leaf, the latter is changed into thin black scales, with the formation of cuprous or ferrous chloride, respectively: nitric acid extracts no silver from these scales; but by prolonged contact with cupric or ferric chloride, they become converted into argentic chloride. Wetzlar was the first to prove that the blackening of argentic chloride in sunlight is attended with the evolution of chlorine; but, as Scheele had found hydrochloric acid to be a product of such blackening, it was inferred that moisture was essential to the action, which, as Berzelius remarks, was an error.[4] (See p. 62 in the sequel.)

Chloride of Silver, AgCl [idem].

Silver combines at the ordinary temperature with gaseous chlorine, without incandescence, and with chlorine dissolved in water, and the product is chloride of silver (argentic chloride). It is an interesting lecture experiment to prepare the chloride by loosely filling a large bottle with silver leaf, and then conveying a stream of chlorine through a glass tube to the bottom, so as to displace the atmospheric air; after which the mouth of the bottle is closed. In a short time the leaf will be entirely converted into white translucent chloride of silver, without shrinking or changing its form. Chloride of silver is usually prepared by adding hydrochloric acid or chloride of sodium to an aqueous solution of nitrate of protoxide of silver, commonly termed nitrate of silver. It is thrown down as a dense curdy white amorphous substance, of which the precipitation is greatly hastened by stirring, shaking, or heating. Chloride of silver is also formed when gaseous chlorine is passed into aqueous solutions of salts of silver; but generally in this case there is also produced, at the same time, some hypochlorite of silver, which, however, is quickly resolved into chloride and chlorate of silver.[5] It crystallizes in the cubical system. It is stated, on the authority of Karsten, that the sp. gr. of amorphous chloride of silver is 5·501; after blackening by light, 5·567; and after fusion, 5·458, or, according to Boullay, 5·548:[6] Rodwell found the sp. gr. of a specimen which had been once fused to be 5·405, and that of a specimen which had been often fused to be 5·505.[7]

Obtained by precipitation, washing and drying at 100° C., chloride of silver is a white powder, perfectly anhydrous. It is stated that

[4] Berzelius, Tr. de Chimie, 1847. 4 p. 260; Handwörterb. d. Chem. 1859. 7. p. 941; Carl Wilhelm Scheele, sämmtliche physische und chemische Werke, nach dem Tode des Verfassers gesammlet, und in deutscher Sprache herausgegeben von D. Sigismund Friedrich Hermbstädt. Berlin, 1793. 1. pp. 135–137. The records of Scheele's experiments on this and every other subject which he investigated, well deserve the attention of chemists of the present day.

[5] Handwörterbuch der Chemie, 1859. 7. p. 935.

[6] Idem, p. 937.

[7] Proceedings of the Royal Society, 1876. 25. p. 291.

when heated to 260° C.,[8] or about the melting-point of lead, it at first becomes lemon-yellow coloured, and then melts into a thin red liquid; but, according to Rodwell, its melting-point is near 360° C.[1] In the molten state it rapidly permeates the substance of ordinary clay crucibles. At a strong red-heat, it volatilizes in dense white smoke. According to Malaguti and Durocher, "Chloride of silver *per se* requires a very elevated temperature for its volatilization, and, besides, it volatilizes very slowly in a closed vessel on account of the feeble tension of its vapour."[2] After fusion and solidification, it has a waxy or horn-like appearance, is translucent, crystalline in fracture, easily sectile, and when in very thin plates flexible, transparent, and apparently colourless though pale yellowish grey when in mass: it emits no cracking sound during solidification. In this state it was designated by the old chemists *horn-silver* or *luna cornea*. When cooled in mass, chloride of silver may be turned in a lathe, and snuff-boxes have been made out of it.[3] I have received from my friend Mr. W. C. Roberts, of the Mint, a singular specimen of chloride of silver, resembling *horn-silver* in appearance, which was found, after the lapse of about three weeks, at the bottom of a vessel containing a strong solution of nitrate of silver, with free nitric acid, to which hydrochloric acid had been added: it is in the form of a thin plate.

Kuhlmann obtained chloride of silver, resembling the native chloride, by the following process:—A tube, filled with a solution of nitrate of silver, is closed with a porous plug of asbestus or pumice, and then immersed, with the mouth downwards, in hydrochloric acid; upon the plug there is gradually deposited chloride of silver, which is described as dendritic in form, warty, translucent, conchoidal in fracture, glasslike in substance, and having a certain degree of softness, like the native chloride.[4]

So great is the insolubility of chloride of silver, that water containing 1–113,000,000th of hydrochloric acid is rendered milky by the addition of nitrate of silver; but when it contains only 1–227,000,000th, the action is almost insensible.[5] Mulder, however, asserts that silver may be detected, by the formation of chloride, in water containing, at the ordinary temperature, 1–1,000,000th of its weight of silver in solution, but that it cannot be so detected in water containing half that proportion of silver in solution.[6] It dissolves in ammonia-water, but less readily, after having been boiled with water, and by slow evaporation is deposited in small cubes and octahedra; in aqueous solutions of hyposulphite of soda in excess, but not without being decomposed; in cyanide of potassium or sodium and other soluble cyanides; in a concentrated solution of sulphocyanide of potassium, from which solution water precipitates crystalline sulphocyanide of silver;[7] in a much less degree, yet notably, in hot hydrochloric

[8] Berthier, Tr. des Ess. 2. p. 788.
[1] Proceedings of the Royal Society, 1876. 25. p. 291.
[2] Recherches sur l'Association de l'Argent aux Minéraux Métalliques, etc. 1850. p. 315.
[3] Aikin's Dictionary, 2. p. 317.
[4] Handwörterb. der Chemie, 1859. 7. p. 935.
[5] Pfaff. Quoted by Berzelius, Tr. de Chim. 4. p. 261.
[6] Jahresber. 1858. p. 626.
[7] Chemical Gazette, 1851. 9. p. 387.

acid and a boiling strong aqueous solution of chloride of sodium or potassium, and subsides in great measure, but not wholly, on cooling; and in aqueous solutions of other chlorides which do not exert any decomposing action upon chloride of silver.

According to Millon and Commaille, chloride of silver is insoluble in a solution of chloride of calcium, or chloride of zinc;[1] but this statement is opposed to the observations of A. Vogel, as also to those of H. C. Hahn, chemist to the Silver Smelting and Refining Works, Wyandotte, Michigan, United States of America.

Vogel prepared solutions of various chlorides in water, saturated at ordinary atmospheric temperatures, by boiling an excess of the salts in water, and after cooling pouring off the supernatant liquors. Into equal quantities of these solutions, respectively, he let fall from a finely-graduated burette a normal silver solution, until decided and persistent turbidity was produced. His results are recorded in the following table:[2]—

TABLE OF SOLUBILITY OF CHLORIDE OF SILVER IN COLD AQUEOUS SOLUTIONS OF VARIOUS CHLORIDES.

Chloride employed.	Weight in grammes of chloride of silver dissolved in 100 cubic centimetres of solution.	Weight of chloride required to dissolve 1 part by weight of chloride of silver.
Chloride of Potassium ...	0·0472	2122
„ Sodium	0·0950	1050
„ Ammonium ...	0·1575	634
„ Calcium	0·0930	1075
„ Magnesium ...	0·1710	584
„ Barium	0·0143	6993
„ Strontium	0·0884	1185

Hahn's results are recorded in the next table:[3]—

TABLE OF SOLUBILITY OF CHLORIDE OF SILVER IN AQUEOUS SOLUTIONS OF VARIOUS CHLORIDES.

Formula of salt.	Percentage of salt in solution.	Saturated at (Centigrade scale).	Percentage of chloride of silver dissolved.	Percentage of silver in the solution.	Specific gravity.	Temperature (Centigrade scale).	Grammes of silver in 100 cubic centimetres of solution.
KCl [idem] ...	24·95	19·6°	0·0776	0·0584	1·1774	19·6°	0·0688
NaCl [idem] ...	25·96	„	0·1053	0·0793	1·2053	„	0·0956
NH^4Cl [idem]	28·45	24·5°	0·3397	0·2551	1·0835	30·0°	0·2764
CaCl [$CaCl^2$] ...	41·26	„	0·5713	0·4300	1·4612	„	0·6283
MgCl [$MgCl^2$]	36·35	„	0·5313	0·3999	1·3350	„	0·5399
BaCl [$BaCl^2$] ...	27·32	„	0·0570	0·0429	1·3017	„	0·0558
FeCl [$FeCl^2$] ...	30·70	...	0·1686	0·1269	1·4199	20·0°	0·1802
Fe^2Cl^3 [Fe^2Cl^6]	37·48	...	0·0058	0·0044	1·4472	21·4°	0·0004
MnCl [$MnCl^2$]	43·85	24·5°	0·1996	0·1499	1·4851	30·0°	0·2226
ZnCl [$ZnCl^2$] ...	53·34	...	0·0134	0·0101	1·6005	„	0·0162
CuCl [$CuCl^2$] ...	44·48	24·5°	0·0532	0·0399	1·5726	„	0·0627
PbCl [$PbCl^2$] ...	0·99	„	0·0000	0·0000	1·0094	„	0·0000

[1] Jahresber. 1863. p. 284.
[2] Wagner's Jahres-Ber. 1874. 22. p. 481.
[3] Transactions of the American Institute of Mining Engineers (May 1873 to February 1874), 2. p. 99.

The numbers in the second column of Vogel's table are comparable with those in the last column of Hahn's table. It will be perceived that the results of these observers differ in some instances considerably.

The solvent action of a saturated cold aqueous solution of chloride of calcium on chloride of silver has been experimented on in my laboratory by E. Jackson. A measured quantity of the solution, to which excess of chloride of silver had been added, was taken out from time to time, and the silver precipitated therefrom by sulphuretted hydrogen. The results are as follow :—

100 cubic centimetres	contained after	2 days	0·0538	gramme of silver.
do.	do.	5 do.	0·0576	do.
do.	do.	10 do.	0·0753	do.
do.	do.	21 do.	0·1134	do.
do.	do.	2 months	0·1426	do.

According to Becquerel, one litre of a saturated solution of common salt, at the ordinary temperature, dissolves 0·807 gramme of chloride of silver.[4]

The following information may be useful in practice to the metallurgist :—100 parts by weight of an aqueous solution of chloride of sodium, saturated at 15·6° C. and 100° C., contain 26·34 and 26·61 parts of salt, respectively : the specific gravities of these solutions at 15·6° C. are 1·20403 and 1·20693, respectively : the specific gravity of the salt at the same temperature is 2·06.[5]

When at ordinary temperatures a solution of nitrate of silver, a little diluted, is poured, drop by drop, into concentrated hydrochloric acid, and the whole is rapidly stirred, the chloride of silver, which forms, dissolves so rapidly at first that often it is difficult to perceive it. The proportion of chloride of silver, which thus dissolves, may exceed 0·5% of the weight of the hydrochloric acid employed. On the addition of water the solution becomes turbid, and the turbidity at first increases with the quantity of water added. But it is difficult to precipitate in this manner the whole of the chloride of silver.[6] A. Vogel has experimented on the solubility of chloride of silver in hydrochloric acid, and obtained the results which are shown in the following table :[7]—

TABLE OF SOLUBILITY OF CHLORIDE OF SILVER IN HYDROCHLORIC ACID.

Strength of the acid employed.					Weight in grammes of chloride of silver dissolved in 100 cubic centimetres of hydrochloric acid.	Weight of anhydrous hydrochloric acid required to dissolve 1 part by weight of chloride of silver.
Hydrochloric acid,	sp. gr. 1·165,	cold,	not diluted	... ...	0·298	336
,,	,,	,,	diluted (10 c. c. with 10 c. c. of water)		0·056	1785
,,	,,	boiling,	,, ,, ,,		0·56	178
,,	,,	cold,	,, (10 c. c. with 20 c. c. of water)		0·018	5555
,,	,,	,,	,, (10 c. c. with 30 c. c. of water)		0·0089	11235
,,	,,	,,	,, (10 c. c. with 50 c. c. of water)		0·0035	28571

[4] Traité d'Électricité et de Magnétisme, etc. : par MM. Becquerel (père et fils), 1855. 2. p. 372.

[5] D. Page and A. D. Keightley. Jahresber. 1872, p. 25.

[6] Pierre, Compt. rend. 1871. 73. p. 1090.

[7] Op. cit. p. 482.

The following observations by Stas may help to elucidate the preceding statements regarding the solubility of silver in different menstrua.[8] The subject is of considerable importance at the present day, when wet methods are largely employed in the extraction of silver, as well as in assaying the metal.

Stas has investigated the cause of the anomaly met with in estimating silver by Gay-Lussac's method (*i.e.*, in titrating a solution of nitrate of silver by an alkaline chloride, a point arrives at which a slight precipitate is produced by the addition of a drop either of the alkaline chloride or of nitrate of silver). Stas finds that chloride of silver is not in all cases perfectly insoluble in pure cold water; but that the degree of solubility varies with the physical condition in which the chloride exists, and with the temperature.

According to Stas, chloride of silver may exist in either of the four following states:—(1) gelatinous; (2) caseous (*caséeux*), flaky (*flocconneux*); (3) pulverulent; and (4) granular, scaly, crystalline, fused. The solubility of the chloride is greatest when in the flaky state, as precipitated, in the cold, from a sufficiently dilute solution of silver; the solubility diminishes as the flakes shrink when left to themselves, or as they are rendered pulverulent by long agitation with water. Flaky or pulverulent chloride of silver dissolved in water, pure or acidified by nitric acid, is precipitated by the addition of a salt of silver, or of hydrochloric acid or an alkaline chloride. Three units of silver or of chlorine are required to precipitate one unit of the dissolved chloride of silver. The precipitation of chloride of silver by the two last-named agents appears to me somewhat anomalous.

The solution of the chloride is wholly effected by pure, or acidified, water, as the case may be; and is not caused by the soluble salt formed simultaneously with the chloride of silver (*e.g.*, nitrate of soda). The presence of nitric acid in the water does not affect the solubility of flaky chloride of silver; but it increases the solubility of the pulverulent chloride in proportion to the quantity of acid present. The precipitation of the dissolved chloride is the exclusive result of its insolubility in the solution formed by adding an excess either of the silver salt or of the alkaline chloride. The granular, scaly, and crystalline chloride of silver is perfectly insoluble in cold water.

The use of an alkaline bromide or iodide, if heating be avoided, obviates the difficulty experienced in following Gay-Lussac's method of estimating silver. This appears to be due to the perfect insolubility of bromide and iodide of silver in cold water.

Chloride of silver is perceptibly soluble in a warm aqueous solution of tartaric acid, and to a less extent in a cold one;[9] and in a slight degree at ordinary temperatures in aqueous solutions of the nitrates of soda, potash, lime, magnesia, and ammonia, but notably more with the aid of heat, insomuch that "hot solutions which are perfectly clear become strongly clouded as they cool."[1] The

[8] Compt. rend. 1870. 73. p. 998. [9] Mulder, Storer's Dict. p. 179.
[1] Idem.

quantity dissolved increases with that of the nitrate of soda present, as well as with the quantity of water. It dissolves in considerable quantity in a cold aqueous solution of mercuric nitrate, and to a much greater extent in a hot one;[2] and from such a hot saturated solution, on cooling, pure chloride of silver is deposited in brilliant yellowish-white crystals: on the addition of an excess of hydrochloric acid, chloride of sodium, chloride of ammonium, or nitric acid, the whole of the silver is thrown down in the state of chloride, and the mercury is also converted into chloride: acetate of soda likewise precipitates the silver in the state of chloride, with the formation of mercuric acetate and of nitrate of soda.[3] It is insoluble in dilute or strong nitric acid, whether cold or hot; but, according to Pierre, when nitric acid is distilled with a small quantity of pulverulent chloride of silver, the latter gradually disappears, but this is no longer a case of simple solution, for crystallized nitrate of silver instead of the chloride is found in the retort when the operation is nearly finished:[4] it is also insoluble in dilute or strong cold sulphuric acid, but is decomposed when boiled with the latter; and in a cold, as well as hot, aqueous solution of sulphurous acid.[5]

With respect to the solution of chloride of silver in ammonia-water, it is necessary to state, by way of warning, that a fulminating compound is deposited on boiling such a solution; whereas by evaporation at a gentle heat the chloride separates in the form of pearly scales, resembling certain varieties of native chloride of silver. The whole of the chloride of silver is precipitated unchanged by neutralizing the ammonia with an acid.[6] Sulphide of silver is thrown down from a solution of chloride of silver in ammonia-water by sulphuretted hydrogen and alkaline sulphides.[7]

A striking property of chloride of silver prepared by the usual methods is that of becoming purplish-grey, and ultimately black by exposure to daylight. But that which I prepared many years ago by the action of gaseous chlorine on silver leaf does not blacken even on exposure to direct sunshine, and it is now as white as at first. Spiller, however, obtained an opposite result (Phil. Mag. 1860. 19. p. 186). When chloride of silver is precipitated in intermixture with a small quantity of mercurous chloride, it is not discoloured by light. Field has published the following interesting fact on this subject. He analysed a mineral from Bolivia, which he found to consist of 78·12% of silver, 12·01% of chloride of silver, 9·34% of ferric oxide, and 0·40% of cobalt; and while the chloride of silver existing in the mineral blackened immediately in sunlight, that which was produced in the analysis (in which the silver was determined as chloride) remained perfectly white after having been exposed to sunlight during many days. Field also directs attention to the chloride of silver, which was exposed in a moist state to the

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[2] Wackenroder, Liebig, and Mulder. Handwörterbuch der Chemie, 1859. 7. p. 939.

[3] Handwörterb., 1859. 7. p. 939.

[4] Compt. rend., 1871. 73. p. 1090.

[5] Mulder, Storer's Dict. p. 179.

[6] Berthier, Tr. des Ess. 2. p. 789.

[7] Idem, p. 790.

direct rays of the sun for a month without blackening, and which Liebig prepared in the following manner:—The precipitate of chloride of silver, which is formed on mixing solutions of nitrate of silver and chloride of mercury (mercuric chloride), was boiled in the liquid in which it originated, when it partially dissolved, owing to the presence of the mercuric nitrate resulting from the reaction between the two salts above named. After filtration, and on cooling, chloride of silver was deposited in crystalline grains, which were washed on a filter until no trace of mercury passed through; and this was the chloride of silver which remained unchanged in sunlight.[8]

When chloride of silver is enclosed in a tube of colourless glass containing atmospheric air and hermetically sealed, and then exposed to solar light, it blackens, but recovers its original whiteness on being kept in the dark. The same result is obtained if chlorine is substituted for atmospheric air, except that blackening in the light takes place more slowly, and subsequent bleaching in the dark more quickly. In 1844 I used tubes containing chloride of silver in chlorine, some with and some without the presence of aqueous vapour, for determining the relative intensity of the chemical action or actinic power of solar light. A tint, painted with a permanent colour, so as to resemble as nearly as possible that acquired by chloride of silver at a given stage of its discoloration by light, is required as a standard of comparison. The time which elapses between the moment of exposure of such a tube to light, and that of the occurrence of the degree of blackening corresponding to the painted standard, is a measure of the intensity of the chemical action of the light. The advantage of such an instrument is, that identically the same chloride of silver is operated upon under identically the same conditions in all experiments made with it; for after use, it has only to be left in the dark for some time in order that the blackened chloride of silver may be rendered white. It would be requisite to ascertain what might be the effect of temperature upon the rapidity of discoloration, and to make corrections accordingly. I proposed that a number of small tubes prepared as above described should be kept in a case ready for use by photographers.

It has been inferred, on the one hand, that the product of the decomposition of chloride of silver by sunlight is dichloride, Ag^2Cl [idem]; and, on the other hand, that it is a mixture of metallic silver and chloride. This is an exceedingly interesting point, of which the consideration would be out of place in this work.

On certain supposed double chlorides of silver.—It is stated that boiling concentrated solutions of the chlorides of potassium, sodium, and ammonium dissolve chloride of silver, and deposit it on cooling in combination with the alkaline chloride. These double salts, so

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[8] Chemical News, 1873. 27. p. 175. Mr. Field informs me (Feb. 6. 1877) that "Löwig" was by mistake substituted for "Liebig."

called, may be thus obtained in a crystalline form, usually cubical; but they are decomposed by water, when the chloride of silver is left undissolved.[9]

Wetzlar, in 1827, announced that he had discovered a crystallized compound of the chlorides of silver and sodium, by boiling a highly concentrated or saturated aqueous solution of the latter salt with more of the former than it could dissolve; or by adding nitrate of silver to the boiling solution of chloride of sodium until some chloride of silver remained undissolved. He states that "by the analysis of this double salt he had not obtained any decided results worth communicating;" that it could exist only in a very concentrated solution of chloride of sodium, and was decomposed by a weaker one, as well as by water, which separated the chloride of silver in numerous voluminous flocks; that it was not in the least affected by exposure to the most intense sunlight; and that not the slightest reduction of silver was caused by the addition of ferrous sulphate to the solution of chloride of sodium containing the double salt. He adds that some further experiments had convinced him that chloride of potassium, chloride of calcium, and other "electropositive metallic chlorides," combined with chloride of silver and produced compounds analogous to that above described with chloride of sodium.[1]

The following experiments upon chloride of silver and chloride of sodium have been made in my laboratory by H. Louis (1876):—

I. A mixture of 47·8 grains of chloride of silver and 117 grains of rock-salt (*i.e.* in the ratio of 1 equivalent of the former to 6 equivalents of the latter) was kept fused, at a low red-heat, for 20 minutes, in a glass tube placed vertically in a crucible. The fused mass was allowed to cool in the tube. It was highly crystalline, apparently homogeneous, of a pale reddish tint (probably due to a trace of impurity), and had a decided metallic taste; on exposure to sunlight the whole mass became bluish-black. When put into water, chloride of sodium dissolved and chloride of silver was left.

II. A hot saturated solution of rock-salt, containing chloride of silver dissolved, was kept heated in an open vessel, when colourless, transparent, cubical crystals, resembling those of chloride of sodium, were obtained. These crystals had a saline and decidedly metallic taste, and did not change in colour by exposure to sunlight. Their composition was found to be as under:—

	Per cent.
Chloride of silver	1·74
Chloride of sodium	97·69
	99·43

This substance does not appear to have any definite atomic constitution. A crystallized substance consisting of chloride of silver and chloride of sodium is met with in nature, of which an account will be found in the sequel, in the article on the Ores of Silver.

[9] Berzelius, Tr. de Chim. 4. p. 263.

[1] Schweigger's Jahrbuch der Chemie und Physik, 1827. 21. p. 371, and 1828. 23. p. 97.

Chloride of silver and ammonia, $AgCl+3NH^3$ [idem].—It is prepared by subjecting dry chloride of silver to the action of dry ammoniacal gas. It is a white powder, containing 17·91% of ammonia, which escapes gradually on exposure to the air.[2]

MODES OF FORMATION OF CHLORIDE OF SILVER.

This is a subject which demands careful study, in connection with various metallurgical processes for the extraction of silver from its ores and certain argentiferous products. In the following account the modes of formation, previously described, will simply be mentioned.

FORMATION OF CHLORIDE OF SILVER FROM METALLIC SILVER.

By chlorine.—When metallic silver is exposed at ordinary temperatures to gaseous chlorine, dry or moist, or to the action of chlorine dissolved in water, chloride of silver is produced. The action, however, is only superficial (except when the silver is in the state of leaf or is in fine powder), owing to the protection afforded to the silver by the encrusting chloride. Chloride of silver is rapidly formed by the action of hydrochloric acid in the presence of various oxidized substances, such as peroxide of manganese, arsenic acid, minium, etc.; in which cases chlorine is disengaged.[3]

By hypochlorous acid and hypochlorites.—By the action of hypochlorous acid gas, or of its aqueous solution on finely-divided metallic silver, when oxygen is evolved:[4] thus,—

$$Ag+ClO=AgCl+O \quad [2Ag+Cl^2O=2AgCl+O].$$

By hydrochloric acid.—Chloride of silver is formed when hydrochloric acid gas, dry or moist, is passed over red-hot metallic silver: thus,—

$$Ag+HCl=AgCl+H \quad [\text{idem}].$$

Yet, conversely, when hydrogen is passed over sufficiently heated chloride of silver, the latter is completely reduced: thus,—

$$AgCl+H=Ag+HCl \quad [\text{idem}].$$

This mode of formation is applied in a singular old process for the extraction of silver from alloys of gold and silver, which will be described in due course.

Chloride of silver, it is stated, is formed at ordinary temperatures, when metallic silver is kept in aqueous hydrochloric acid, hydrogen being evolved;[5] and more rapidly when it is subjected to the combined action of the same acid and atmospheric air.

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[2] H. Rose. Berzelius, Tr. de Chim. 4. p. 263.

[3] The Chemical Essays of Charles William Scheele, translated (by Dr. Beddoes) from the *Transactions* of the Academy of Sciences at Stockholm. With additions. London, 1786. p. 172.

[4] Balard. Gmelin's Handb. 6. p. 163.

[5] Proust. Idem.

Fischer satisfied himself that silver dissolves in hydrochloric acid, and that its solubility therein is much promoted by the presence of another metal; for example, iron or copper. Faraday and Stodart also observed that, in analysing their supposed alloy of silver and steel, silver was attacked and dissolved by hydrochloric acid, contrary to the usual opinion. Wetzlar, however, doubts whether the *pure* acid has any solvent action on *pure* silver; and, in support of this doubt, adduces the results of his experiments on the action of dilute sulphuric acid on silver, an account of which has been given at p. 45 of this volume.[6] It is certain that if there be any such action it must take place very slowly.

By chloride of ammonium.—Chloride of silver is formed when the vapour of chloride ammonium is passed over silver heated to redness; and, conversely, chloride of silver is reduced to the metallic state when heated to redness in a current of the vapour of chloride of ammonium.[7] The following equations show these two opposite reactions:—

$$Ag + NH^4Cl = AgCl + NH^3 + H \text{ [idem]}.$$
$$3AgCl + NH^4Cl = Ag^3 + N + 4HCl \text{ [idem]}.$$

When an aqueous solution of chloride of ammonium is evaporated upon metallic silver, a compound of the two chlorides is formed, with, at the same time, the evolution of a little ammonia. In contact with silver this compound is said to be changed into dichloride of silver (argentous chloride), so that, on washing with water, that salt is left as a deep black spot.[8] No action, however, upon silver is produced by a solution of chloride of ammonium, provided air be excluded; but when air is not excluded, chloride of silver is formed and ammonia volatilizes.[9]

Wetzlar found that an aqueous solution of chloride of ammonium left no black coloration on a plate of chemically pure silver, but that blackening occurred when a piece of copper was laid in the solution on the silver. Hence he inferred that the blackening of silver plate by contact with the above-mentioned solution was due to the copper which is always present in such plate.[1]

By certain Metallic Chlorides:—1. *By chloride of sodium.*—When silver is subjected to the action of an aqueous solution of this chloride, with access of atmospheric air, chloride of silver is formed; and in this way, it is supposed, silver coins have been more or less converted into chloride of silver by long immersion in sea-water.[2]

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[6] Schweigger's Jahrbuch der Chemie und Physik, 1828. 22. p. 476.

[7] Berzelius, Tr. de Chim. 4. p. 262.

[8] Idem, 4. p. 261.

[9] Vogel. Berzelius' Jahres-Ber. 1836. 15. p. 170.

[1] Schweigger's Jahrbuch der Chemie und Physik, 1828. 22. p. 467.

[2] Gmelin's Handb. 6. p. 163. I have received from Dr. Boycott a Mexican dollar, with this note attached:—"Taken from the steamer 'Pacha' five years after she had been wrecked in the Straits of Malacca. Silver of the value of 50,000*l.* was recovered from this wreck, and the whole of it was coated with sulphide of silver." The coating of sulphide on the dollar given to me was exceedingly thin. On the reverse were small rounded and irregular thin patches, radiated in

By boiling silver leaf in a concentrated solution of common salt, the liquid, according to Wetzlar, becomes slightly alkaline and acquires a decided taste of silver in solution.[3]

According to Henri Sainte-Claire Deville, silver dissolves with extreme rapidity in [an aqueous solution of] common salt, but in small quantity. By heating for a few minutes a solution of common salt in a crucible of *pure* silver, the saline solution acquires the property of turning red litmus-paper blue, which indicates the presence of caustic soda.[4] It is well known that when silver salt-cellars are used, the surface of the metal in contact with the table salt becomes corroded and blackened; and, consequently, such articles should be gilded internally.

In order to ascertain whether any chloride of silver is produced by contact of metallic silver with an aqueous solution of chloride of sodium, without access of atmospheric air, the following experiments have been made in my laboratory by E. Jackson (1875). An aqueous solution of chloride of sodium, made with the purest rock-salt, and boiled for a few minutes in a silver crucible, turned red litmus-paper blue. But it was afterwards found that the solution of salt, before it came into contact with silver, gave the same alkaline reaction. In order to avoid error on this point, water was used which had been distilled in a platinum vessel, and the solution was made in a platinum crucible. Nevertheless, it was proved, that in the foregoing experiment silver existed in the solution of salt, which had been boiled in the silver crucible; for sulphide of silver was precipitated from this solution by sulphuretted hydrogen. In a second experiment a piece of silver was put into a flask containing a solution of chloride of sodium, prepared as above stated, and the solution kept boiling for two hours, great care being taken completely to exclude atmospheric air all the while. The result was that in this case *no sulphide of silver was precipitated* from the boiled solution by sulphuretted hydrogen. Hence it may be concluded that chloride of silver is not formed when a solution of chloride of sodium is boiled in contact with silver, unless atmospheric oxygen has access.

The following experiments on the action, at ordinary temperatures, of a solution of chloride of sodium, with access of atmospheric air, on the British monetary alloy of silver and copper, which contains 7·5% of copper, have been made in my laboratory by C. Tookey (1869):—

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structure, somewhat waxy in lustre, pale yellowish brown, and here and there green. I suspected them to be chloride of silver, but they proved to be only carbonate of lime. Besides the dollar, I received several detached portions of the black encrusting matter much thicker than the coat on the dollar. On some the surface presented little conical pimples, some sharply pointed, and others with the points broken off, showing the interior to be hollow. The pimpled surface was the outer one. The crust consisted mainly of sulphide of silver; it effervesced with dilute hydrochloric acid, and the solution contained chiefly lime, with small quantities of copper and of iron. I do not understand how the sulphide of silver was formed under the conditions mentioned.

[3] Berzelius, Tr. de Chim. 4. p. 264.

[4] De l'Aluminium, ses Propriétés, sa Fabrication et ses Applications. Par M. H^te. Sainte-Claire Deville. Paris, 1859. p. 33.

A new florin, dated 1868, was rolled out thin and cut into two pieces, one of which was annealed in the flame of a spirit lamp, while the other was left unannealed and cleaned with an aqueous solution of caustic potash. The surface of the annealed piece was blackened, owing to the oxidation of copper. Both pieces were placed in a solution of chloride of sodium to which air had access. The following statement shows the weights of the pieces before the experiment commenced, and the loss on treating each piece with water and ammonia-water successively, after the experiment had continued for eight months:—

March 13, 1869.

	Grains.
The annealed piece (A) weighed	85·96
The unannealed piece (B) weighed	88·53

November 15, 1869.

			Grain.	Per cent.
A, after boiling in water, weighed	85·22	... loss =	0·74	
B, do. do. do.	87·67	... do. =	0·86	
A, after cleaning with ammonia-water, weighed	84·72	... do. =	1·24	... 1·442
B, do. do. do.	87·02	... do. =	1·51	... 1·705

The ammonia-water used for cleaning acquired a pale blue tint.

The following observations on the changes which silver coins have undergone after long burial in the earth may here be appropriately introduced. I received (June 1875) from my friend Mr. John Evans, the well-known archæologist, one of a number of silver coins of Edward the Confessor, which had become brittle. It was partially coated with a thin dark-grey crust, pitted with numerous small circular cavities, while the rest of the surface was bright. The weight of the whole coin was 21·02 grains. It was stated to have been annealed before it reached me. A piece of the coin was examined which was partly encrusted and partly bright. It was treated repeatedly with dilute ammonia-water, by which treatment flakes of what appeared to be metallic silver were detached. These, together with the residual metal, were washed, dried, and weighed. The ammoniacal solution contained chlorine, silver, copper, with traces of sulphuric acid, and was analysed quantitatively. The results, which were obtained by my assistant R. Smith, are as follow:—

	Per cent.
Coin, with detached flakes of silver.....	88·36
Chloride of silver	10·50
Oxide of Copper, CuO [idem]	0·73
Oxychloride of copper (see formula, p. 79) *	0·41
Sulphuric acid	traces
	100·00

* The chlorine in excess of that present in the chloride of silver is assumed to have existed in this state of combination. It was not till after the analysis had been completed that I was informed that before reaching me the coin had not only been annealed, but immersed for some hours in ammonia-water.

In some antique silver vessels found at Hildesheim in October

1868, Schertel noticed a very considerable change in the metal.[4] Every trace of malleability and toughness had disappeared; the smallest pieces could be broken off easily, and the fracture had no longer the "fibrous appearance" (?) of a hammered metal, but was mostly granular. Schertel tried experiments on some fragments, weighing a few grammes, with a view to ascertain the causes of this change.

The exterior of the vessels, where they were in contact with the clay in which they were imbedded, was encrusted with chloride of silver, of varying thickness. On closer examination the crust proved not to be homogeneous. Next to the metal itself was a layer, nearly black, mostly very thin, which could not be cut, but crumbled under the knife; and which analysis showed to consist of 87·0% of silver and 12·8% of chlorine. (Argentous chloride, Ag^2Cl [idem], contains 85·89% of silver and 14·11% of chlorine.) Over this layer was a thicker, paler, and sectile one, which proved to be horn-silver, AgCl [idem]; and which analysis showed to consist of 75·43% of silver and 24·51% of chlorine. Between the inner layer of argentous chloride and the unattacked silver was a little, dark, feebly-lustrous powder, soluble in aqua-regia, and which gave a purple precipitate with oxalic acid,—a proof that it was gold. One fragment, with the attached chloride of silver, weighed 1·665 gram., and without it 1·150 gram.; so that, in parts, over 25% of the metal had entered into combination with chlorine. Of the following analyses, I. and II. of pieces of the metal from two different vessels, were made by Schertel, and III. was made in the laboratory at Göttingen:—

	I.	II.	III.
Silver	94·00	98·20	94·78
Gold	2·70	trace	3·18
Copper	3·26	1·56	1·92
	99·96	99·76	99·88

The small proportion of copper seems to indicate that this metal was accidentally present, and had not been expressly added to the original alloy. But in any case, Schertel remarks, the first cause of the change, which the metal had undergone, was due to the copper; the layer of chloride of silver shows plainly that the water percolating through the clay, and containing chlorides in solution, first changed the copper into cupric chloride, and that this formed with silver argentous and cuprous chlorides. The cuprous chloride was then reconverted into cupric chloride, and again attacked the silver. The clay surrounding the metal kept the liquid in contact with it for a long time; so that, with but little copper, much silver was converted into chloride. The clay retained the chloride of silver like a filter, so that a thick incrustation was formed upon the vessels. As the process went on slowly, the gold (after the particles of silver

[4] Journal für praktische Chemie, 1871. 3. p. 317.

and copper associated with it were converted into chloride) was enabled to deposit itself, as a fine powder, on the still unattacked metal.

The formation of an incrustation of chloride of silver, by some such process as that suggested by Schertel, is conceivable; yet, without the presence of copper, chloride of silver would be formed under the conditions stated,—namely, the presence of atmospheric oxygen and dissolved chlorides, of which chloride of sodium must surely have been one. But the interesting fact—namely, the entire absence of malleability and toughness in the *unattacked* metal beneath —remains unaccounted for. This result may possibly be due to a molecular change in the metal. Schertel rolled a franc-piece into thin foil, and kept a portion immersed in a solution of chloride of sodium for six months: at the end of that time it was found to be brittle, especially in the thinner portions, and had lost 27·7% of the copper present.[6] In this case it is supposed that the brittleness was due to the abstraction of the copper from the metal.

I am not aware whether trustworthy experiments have been made concerning the action of aqueous solutions of the chlorides of calcium, barium, magnesium, and other allied chlorides on metallic silver, yet there can be little doubt that it would be similar in kind to that of chloride of sodium.

When metallic silver is heated to bright redness in contact with chloride of sodium and with access of atmospheric air, chloride of silver is produced; and in proof of the fact the following experimental evidence is adduced. Winkler triturated fine silver leaf with common salt, and exposed this intimate mixture in a scorifier, covered with another inverted scorifier, to bright redness in a muffle during three-quarters of an hour. The silver was found to be thereby changed into chloride. The experiment was repeated with the substitution of silver filings for leaf; but in this case the silver was only partially changed into chloride. At a lower temperature the whole of the silver remained in the metallic state. The covering of the scorifier seemed to have no effect.[7]

Plattner found that on roasting a mixture of finely-divided silver and common salt, with the addition of a large excess either of sesquioxide of iron or protoxide of copper, no more chloride of silver was formed than without such addition.

H. Rose has recorded the following observations on this subject. He made his experiments in suitably covered clay crucibles, manufactured at the Meissen porcelain works, so that atmospheric air could only get very limited access. Silver was kept long melted under common salt in an air-furnace, until the salt had in great part volatilized: the residual salt contained much chloride of silver. The longer the heating, the greater was the loss of silver. The loss in very strongly heating 27·8 grammes of silver with two ozs. (Prussian)[8] of

[6] Wagner's Jahres-Ber. 1871. p. 117.

[7] Winkler, Die Europäische Amalgamation der Silbererze und silberhaltigen Hüttenprodukte. Freiberg, 1848. p. 166.

[8] 4 loth. 2 loth = 451·1 grains, or about 29 grains less than the troy oz. of 480 grains.

common salt during 2½ hours was 0·75 gram. = 2·7% of the silver: the salt had wholly volatilized and the silver solidified without "spitting." On heating 27·05 gram. of silver with 4 ozs. of salt during a shorter time, so as only partially to volatilize the salt, the loss was 0·35 gram. = 1·29% of the silver. The same button of silver was again melted with 3 ozs. of salt, when the loss was 0·3 gram. = 1·12% of the silver. The residual salt contained much chloride of silver. Rose inferred that the sodium of the salt, from which the chlorine of the chloride of silver is derived, is evolved as soda as fast as it is generated, and not that the soda formed combines with the silica of the crucible; for soda and chloride of silver cannot co-exist at the temperature of the experiment; and, moreover, the residual salt was not in the least alkaline. In another experiment 38·9 gram. of silver were melted under 4 ozs. of common salt, and black oxide of manganese was added to the molten mass: the loss was 0·7 gram. = 1·8% of the silver, and no mineral chameleon was produced. He melted silver alloyed with copper (Prussian dollars were used) under common salt, but in this case no chloride of silver was formed, and the residual salt was not in the least degree alkaline. The production of dichloride of copper (cuprous chloride) and evaporation of common salt were much smaller when the experiment was made in the less porous Hessian crucibles. A Prussian dollar melted in a Meissen clay crucible with 3 ozs. of common salt lost 0·43 gram. = 1·93%. The same piece of metal was again kept melted under 3½ ozs. of common salt in a Hessian crucible during about the same time, when the loss amounted to 0·15 gram. = 0·69%. Copper, therefore, prevents the formation of chloride of silver and the consequent loss of silver.[9]

The following experiment on this subject has been made in my laboratory by R. Smith:—Three silver leaves, 4½ inches square, and weighing 1·318 grain, were triturated with 300 grains of the purest rock-salt, and the mixture was kept heated in a scorifier in a muffle for about three-quarters of an hour, at a temperature sufficient to melt the salt. On adding hot water to the product when cold, 0·28 grain of metallic silver was left undissolved. On further dilution with water chloride of silver was precipitated. The results are as under:—

	Grains.
Weight of silver taken	1·318
Ditto left	0·280
Ditto converted into chloride	1·038

Hence 78·76 per cent. of the silver operated upon had been changed into chloride.

2. *By chloride of copper*, CuCl [$CuCl^2$].—I heated a strip of metallic silver to redness, and put it into a glass tube containing an aqueous solution of chloride of copper, which was boiled

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[9] Ueber das Spratzen des Silbers, von H. Rose. Poggendorff's Annalen, 68. p. 283. The preceding statement of Plattner is given on Rose's authority.

and sealed in hermetically (August 3rd, 1853). After two years, during which the tube had been more or less exposed to daylight, the following observations were recorded. The solution was dark brown. The strip of silver was coated with a dark crust, which presented glistening points and under a lens appeared minutely crystalline. At the bottom of the tube were a few detached crystals with distinct triangular faces, which dissolved in ammonia-water and resembled dichloride of copper, Cu^2Cl [Cu^2Cl^2]. The crystalline crust dissolved in aqueous ammonia without communicating the slightest tinge of blue, and, on the addition of nitric acid in excess to this solution, a copious white precipitate of chloride of silver was formed.

An experiment precisely similar to the last was begun at the same time, except that a solution containing chloride of sodium, in addition to chloride of copper, was employed. After two years, during which the tube had been more or less exposed to daylight, the following observations were recorded.[1] The solution was dark brown. The strip of silver was coated with a brown crust, consisting of shining crystalline particles, amongst which, under a lens, I thought I recognized cubical faces. The crystals were much larger than in the last experiment. On scraping off the crust with a penknife, it seemed to have the consistency of horn-silver. The crust dissolved in aqueous ammonia without communicating the slightest tinge of blue; and on adding nitric acid in excess to the solution, a copious curdy white precipitate was produced. On digesting a piece of the strip of silver with adherent crust in nitric acid, somewhat diluted, there was slight action, which seemed chiefly confined to the cut edges, thus showing how effectually the crust prevented contact between the subjacent metal and the acid. The brown solution was treated with nitric acid, heated, and diluted with water, when it became milky. The brown colour shows that cuprous chloride was present (see p. 81).

The results of these experiments agree with those previously arrived at by Karsten, who found that, at temperatures ranging from 12° C. to 20° C., the action took place very slowly without, and very rapidly with, the presence of chloride of sodium.[2]

The reaction is shown in the following equation:—

$$2CuCl + Ag = Cu^2Cl + AgCl.$$
$$[2CuCl^2 + 2Ag = Cu^2Cl^2 + 2AgCl.]$$

According to Karsten, an ammoniacal solution of chloride of copper does not act upon metallic silver.

3. *By sesquichloride of iron.*—When metallic silver is kept immersed in an aqueous solution of this salt, the latter is slowly reduced to

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[1] The point at the sealed end had been broken, and that end afterwards covered with caoutchouc, so that exclusion of atmospheric air may have been imperfect.

[2] Ueber den jetzigen Zustand der Verfahrungsmethoden zur Darstellung des Silbers aus seinen Erzen. Archiv, 2nd series, 1852. 25. pp. 175 et seq. I shall have occasion again to quote from this paper.

protochloride. Berzelius availed himself of this fact in a method of analysis for determining the relative proportions of protoxide and sesquioxide of iron in substances capable of solution in hydrochloric acid. Finely-divided silver, such as is produced by leaving a piece of zinc for some time in contact with a fused cake of chloride of silver, moistened with hydrochloric acid, then breaking up and thoroughly washing and drying the reduced silver, may be used: the action is promoted by keeping the solution heated to 100° C. Frequent shaking is necessary, as the chloride of silver, formed on the particles of metallic silver, prevents contact between the latter and the solution of iron. The reaction is shown by the equation:—

$$Fe^2Cl^3 + Ag = 2FeCl + AgCl.$$
$$[Fe^2Cl^6 + 2Ag = 2FeCl^2 + 2AgCl.]$$

According to Wetzlar, at a certain stage there is formed a black chloride of silver, supposed to be dichloride, which, by prolonged immersion in the solution of sesquichloride of iron, becomes converted into the common white chloride.[2] Heated to the melting-point of chloride of silver, the so-called black chloride is said to be changed into a yellow mixture of metallic silver and chloride of silver.[3] The same chemist states that when a dilute solution of sesquichloride of iron is poured upon silver leaf, the latter almost instantaneously loses its lustre and falls into small spangle-like flakes, of which the powder is black with a slight brown tinge. This product is also the black chloride of silver; and Wetzlar considered it to be a "sub-chloride," identical with that resulting from the action of sunlight on ordinary chloride of silver: it is not acted upon by nitric acid, cold or even hot, if the heating be not too long continued; by the action of ammonia-water, or a solution of chloride of sodium, it is converted into metallic silver, and chloride of silver which dissolves.[4]

We have confirmed the accuracy of the foregoing statement, except that the particles were not spangle-like, and that we found it necessary to use what we should term a strong solution of sesquichloride of iron instead of a dilute one, as prescribed by Wetzlar; but the word "dilute" is always more or less vague.

4. *By chloride of mercury or corrosive sublimate*, HgCl [$HgCl^2$].—Chloride of silver and dichloride of mercury (mercurous chloride) are formed when metallic silver is kept in an aqueous solution of chloride of mercury, as shown by the equation:[5]—

$$2HgCl + Ag = Hg^2Cl + AgCl.$$
$$[2HgCl^2 + 2Ag = Hg^2Cl^2 + 2AgCl.]$$

The following experiment on this subject has been made in my laboratory by C. Tookey:—Six leaves of silver, weighing 2·61 grains

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[2] Gmelin's Handbook, 6. p. 161. For further information concerning this black chloride, consult Gmelin's Handbook. Wöhler has examined it.

[3] Idem.

[4] Schweigger's Jahrbuch der Chemi und Physik. 1828. 22. pp. 474-6.

[5] Vogel. Gmelin's Handbook, 6. pp. 5 161.

were mixed with chloride of mercury, and then water was added, March 15, 1869. The bottle containing the mixture was occasionally shaken, and on October 15, 1869, its contents were collected on a filter and washed. The substance remaining on the filter was grey and somewhat pearly in lustre. A portion of it, when treated with ammonia-water, became black, from the formation of black oxide of mercury, Hg^2O [idem]; and chloride of silver was found in the solution. The proportions of the substances used were such as to form chloride of silver and dichloride of mercury, so that if this reaction had been complete no mercury should have been left in solution, as was practically proved to be the case; for when sulphuretted hydrogen was passed into the filtrate, only a trace of precipitate appeared.

When a mixture of finely-divided silver and chloride of mercury is heated, dichloride of mercury or calomel, Hg^2Cl [Hg^2Cl^2], sublimes, and chloride of silver remains.[6]

FORMATION OF CHLORIDE OF SILVER FROM SULPHIDE OF SILVER.

Attention is particularly invited to the following reactions with sulphide of silver, which relate to the extraction of silver from its sulphuretted ores by the Mexican Amalgamation Process. In 1855, I directed various experiments on the subject to be made in my laboratory by my friend Mr. Dick, at that time one of my assistants, the results of which I now publish for the first time. The sulphide of silver operated upon was prepared by passing sulphuretted hydrogen through an aqueous solution of nitrate of silver, washing the precipitated sulphide with water, digesting it with sulphide of ammonium in order to dissolve any intermixed free sulphur, again washing and thoroughly drying. Not the slightest oxidation of the sulphide occurred during this process. However, the sulphide so produced still retained a trace of free sulphur, which was removed by digestion with an aqueous solution of potash, thoroughly washing with water, and drying. The chloride of copper (cupric chloride) used was prepared by converting electrotype copper into nitrate, the nitrate into oxide (cupric oxide), and the oxide into chloride by digestion with hydrochloric acid, great care being taken to make it neutral. The dichloride of copper (cuprous chloride) was prepared by boiling an aqueous solution of chloride of copper, and free hydrochloric acid, with metallic copper, precipitating the dichloride so formed by the addition of water, and thoroughly washing first with hot and afterwards with cold water. The chloride of sodium used was rock-salt free from sulphuric acid. The materials were exposed in shallow porcelain basins to the action of atmospheric air, at ordinary temperatures when not otherwise stated, but protected from the contaminating vapours of the laboratory. Dick's experiments, Nos. 1 to 5, and 13 to 16, were commenced on the 8th of August, and

[6] Gmelin's Handbook, 6. p. 56.

the examination of the products was commenced on the 15th of September following. The reports of these experiments should at first be read consecutively, omitting the paragraphs under the head of "Remarks."

1. *Sulphide of silver, chloride of sodium, air, and water.*—Moist sulphide of silver was mixed with chloride of sodium. When examined, the sulphide of silver was covered by a thin stratum of strong solution of chloride of sodium; atmospheric air, it will be borne in mind, having been present. The mixture was filtered. The filtrate contained no sulphuric acid. The residue was digested with ammonia-water and filtered. The filtrate was neutralized with nitric acid, but there was no precipitate; and, consequently, *no chloride of silver had been formed.*

2. *Sulphide of silver, chloride of copper (cupric chloride), air, and water.*—Moist sulphide of silver was mixed with an aqueous solution of chloride of copper. When examined, the liquid, as was evident from its colour, contained chloride of copper; but there was a large quantity of deposit of a light-green colour, through which black particles of sulphide of silver were diffused. The mixture was filtered, and nitrate of baryta was added to the filtrate, when almost immediately a slight precipitate was produced, which did not increase on standing. The insoluble residue was washed with water by decantation, then digested with ammonia-water for a minute or two and filtered. The filtrate had a deep blue colour, and the residue was blackish, the greenish deposit having dissolved. On neutralizing the filtrate with nitric acid, *a bulky precipitate of chloride of silver was formed.* The residue was re-digested with ammonia-water, until no more copper or silver was extracted, then thoroughly washed with water, and digested with an aqueous solution of potash.[7] The solution was filtered, and on the addition of nitrate of silver or acetate of protoxide of lead to the filtrate, blackening occurred; and when another portion of the filtrate was neutralized with hydrochloric acid, sulphur was precipitated. Sulphide of silver is not acted upon by such a solution of potash. *Sulphur, therefore, had been separated.*

Remarks.—Boussingault asserts that an aqueous solution of chloride of copper (cupric chloride) has no action on sulphide of silver, even though contact between these substances be prolonged for months; but that immediately after the addition of chloride of sodium decomposition of the sulphide begins and continues until the whole of the silver is changed into chloride, with the formation of an equivalent proportion of sulphide of copper. He says nothing about access of atmospheric air.[8] Karsten states that an aqueous solution of chloride of copper (cupric chloride) has no action on sulphide of silver at ordinary temperatures, at least none was observed even after the lapse of four months, the mixture having been shaken from time

[7] The same solution of potash was kept in a stoppered bottle for use in these experiments.

[8] Recherches sur les Phénomènes chimiques qui se passent dans l'Amalgamation américaine. Ann. de Chim. et de Phys. 1832. 51. p. 350.

to time. But when water was replaced by a saturated solution of chloride of sodium, incomplete decomposition very slowly occurred, with the formation of chloride of silver and dichloride of copper (cuprous chloride), and the separation probably of free sulphur. It is very difficult, Karsten adds, to determine what takes place in such an experiment, because the dichloride of copper (cuprous chloride) acts as fast as it is formed on the sulphide of silver, even though the action is slower than that of the chloride of copper.[3] He says nothing about the access of air, so that the experiment, we may infer, was conducted in a closed vessel. No action, according to Karsten, occurs when an aqueous ammoniacal solution of chloride of copper is used. He operated upon artificially-made sulphide of silver.

Thus, according to both Karsten and Boussingault, the presence of chloride of sodium in the solution, as well as of chloride of copper, is essential to the formation of chloride of silver from sulphide of silver; whereas it was found in the preceding experiment, 2, that the presence of chloride of sodium was not essential. And according to Malaguti and Durocher. the presence of chloride of sodium is not essential, though it causes double the quantity of chloride of silver to be formed in a given time; owing, it is suggested, to the chloride of silver being dissolved in greater or less degree by the solution of chloride of sodium in proportion as it is formed, so as to expose fresh surfaces of the sulphide of silver to the action of the cupric chloride.

The details of their experiments on this point are as follow:—They operated upon pure native sulphide of silver. The mixtures were put into badly-corked bottles, so that air had access; and the bottles were shaken simultaneously from time to time during two months. In each experiment the weight of the sulphide of silver was 0·110 gramme, which corresponds to 0·132 gramme of chloride of silver; and the solution used in one experiment was 30 cubic centimetres of a solution containing 0·300 gramme of cupric chloride, while in the other experiment the same quantity of the same solution was used, with the addition of chloride of sodium. The weight of chloride of silver produced is stated in hundredths of what would have been formed if the whole of the sulphide had been converted into chloride of silver. In the first experiment 34% of chloride was produced, and in the second 65%.[1]

Malaguti and Durocher found that an aqueous solution of cupric chloride decomposed sulphide of silver at ordinary temperatures, without the presence either of air or of chloride of sodium, cuprous and argentic chlorides being formed and sulphur set free.[2]

3. *Sulphide of silver, chloride of copper (cupric chloride), chloride of sodium, air, and water.*—Moist sulphide of silver was mixed with chloride of sodium and an aqueous solution of chloride of copper. When examined, the liquid had the colour of chloride of copper,

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[3] Archiv, 2. s. 1852. 25. p. 182.

[1] Recherches sur l'Association de l'Argent aux Minéraux Métalliques, etc. 1850. p. 405.

[2] Op. cit. p. 248.

and there was a light-green deposit similar in appearance to that formed in the last experiment, in which were diffused undecomposed particles of sulphide of silver. The mixture was filtered and the filtrate was found to contain a *small quantity of sulphuric acid*, resulting possibly from the atmospheric oxidation of the free sulphur in contact with oxychloride of copper. The quantity, however, of sulphuric acid formed was so small that in a practical point of view it may be disregarded. The residue was treated as in the last experiment, and yielded *a bulky precipitate of chloride of silver*; it was also tested in the same manner as in the last experiment, and found to contain *free sulphur*. As the weights of the substances operated upon were not determined, it was not ascertained whether the presence of chloride of sodium favours the decomposition of the sulphide of silver or not. The reactions seem to be substantially the same as in the last experiment.

Remarks.—The solution of cupric chloride in common salt decomposes in the course of a few days stephanite, red silver ores, and fahl-ores, but the latter most slowly: cuprous and argentic chlorides are formed.[8]

4. *Sulphide of silver, dichloride of copper (cuprous chloride), chloride of sodium, air, and water.*—Moist sulphide of silver was mixed with these chlorides. When examined, the liquid had a decided greenish tinge, which it had not at the commencement of the experiment, and there was a deposit similar in appearance to that formed in the preceding experiments. The mixture was filtered. The filtrate contained a very small quantity of sulphuric acid. The residue resembled that in the two preceding experiments, and was found to contain *free sulphur and a considerable quantity of chloride of silver.*

5. *Sulphide of silver, dichloride of copper (cuprous chloride), chloride of sodium, and water, without air.*—An experiment was made with a mixture of sulphide of silver, dichloride of copper (cuprous chloride), and a strong aqueous solution of chloride of sodium, in an air-tight bottle, but *not a trace of chloride of silver was formed.* Atmospheric oxygen, it may therefore be inferred, plays an essential part in the reaction.

The substances used in this experiment having been carefully preserved in a small corked flask since 1855, were examined by me in December 1876. As the cork did not fit tightly air had got access into the interior of the flask, which was filled nearly up to the cork. There was a large amount of deposit, covered by clear deep-green supernatant solution, like that of cupric chloride. This deposit consisted of three layers, but not however very distinctly separated from each other: the lowermost one was light grey—the next much thinner and white,—and the uppermost one the most copious and of mixed white and light-green colours, irregularly veined like what is seen in some specimens of pale-coloured malachite. Very sensible turbidity

[8] Karsten, Archiv, 2. ser. 25. p. 183.

was produced in the supernatant solution by the addition of chloride of barium, thus showing that sulphuric acid had been produced. The precipitate slowly dissolved for the most part in strong ammonia-water, forming a solution of the colour of *aqua cœlestis*. The washed residue was dark-coloured, and when gently warmed emitted unmistakably the smell which sulphur emits when so treated. By digestion with dilute nitric acid the dark colour of the residue disappeared, and only a small portion of it dissolved; the solution had a bluish tint and contained silver, and what did not dissolve was pale yellow sulphur: the inference is that the residue consisted of free sulphur mixed with a small proportion of sulphide of silver. There was not the faintest appearance of any metallic silver.

Remarks.—Malaguti and Durocher, however, state that by the action of a solution of cuprous chloride in chloride of sodium upon sulphide of silver in the presence of air, some chloride of silver is formed, but the silver is chiefly reduced to the metallic state; the copper being converted into oxychloride and sulphide.

The same observers also state that when cuprous chloride (in the solid state) is introduced into a flask containing only sulphide of silver and water, no chloride of silver is formed, but the silver is reduced to the metallic state, and the copper converted into sulphide and cupric chloride. The action is stated to be so much accelerated by heat, that after boiling for "a few instants" nearly the whole of the silver is separated in the metallic state: no mention is made of the presence of air.[4]

The following details concerning the solubility of cuprous chloride in an aqueous solution of chloride of sodium, have been published by Dr. Sterry Hunt, in a pamphlet on "A New Process for the Extraction of Copper from its Ores." A saturated solution of chloride of sodium dissolves more than 16% of cuprous chloride at 90° C., and more than 8% at 40° C.; and a solution, containing 15 parts by weight of chloride of sodium in 100 parts of water, dissolves 10% of cuprous chloride at 90° C., 6% at 40° C., and 3·5% at 14° C. When the above solutions are diluted with water, much of the cuprous chloride is deposited as a white crystalline powder. A solution containing 5 parts by weight of chloride of sodium in 100 parts of water, dissolves only 2·6% of cuprous chloride at 90° C., and 1·1% at 40° C. It is added that the "above figures are approximate, and a little below the results of actual experiment."

6. *Composition of the light-green deposit.*—The light-green deposit produced in experiment 4 was analysed in my laboratory by Tookey in June 1869, the products of the experiment having been carefully preserved in a corked bottle from September 1855 until that date. These products, both liquid and solid, were transferred to a filter; and what did not pass through was washed with water and then dried. Of this dry insoluble substance 10 grains were acted upon by dilute nitric acid, which dissolved most but not the

[4] Op. cit. p. 407.

whole of it. The solution was filtered, and the insoluble residue, after having been washed and dried, was gently ignited, when sulphur was manifestly burnt off. The ignited residue, which consisted of chloride of silver, was moistened with a mixture of nitric and hydrochloric acids, and again heated. To the filtrate nitrate of silver was added, in order to precipitate the chlorine combined with copper. The composition of the washed and dried precipitate in the bottle, which contained the products of this experiment, was found to be composed as follows:—

	Per cent.
Chloride of copper (cupric chloride)	23·07
Protoxide of copper (cupric or black oxide)	42·77
Chloride of silver	23·60
Sulphur, in a free state *	2·47
Water	8·09
	100·00

* Any sulphuric acid which may have been present was not estimated.

From these numbers the following formula may be deduced:—

$$2(CuCl,3CuO.3HO)+AgCl+S.$$
$$[2(CuCl^2,3CuO,3H^2O)+2AgCl+S.]$$

Calculated from this formula the composition of the deposit is as follows:—

	Per cent.
Chloride of copper	22·93
Protoxide of copper	40·59
Chloride of silver	24·51
Sulphur, in a free state	2·73
Water	9·24
	100·00

7. *Composition of artificially made oxychloride of copper.*—The oxychloride of copper formed in this experiment is the same as that which is produced by the joint action of hydrochloric acid and atmospheric air on metallic copper, and which is known by the name of *Brunswick green*. In order to satisfy myself on this point the following experiment was made:—Strips of copper-foil were put into a wide-mouthed bottle, and kept moistened with strong hydrochloric acid, diluted with about its own volume of water. The bottle was closed with a loosely-fitting cork, kept in a warm place, and shaken from time to time. The oxychloride was produced rapidly after it had once begun to form. By this means a considerable quantity of the salt was obtained in the course of a week or two. It was easily washed off the residual unchanged copper. After washing and drying at 100° C., it was analysed by R. Smith, and its composition found to be as follows:—

COMPOSITION OF OXYCHLORIDE OF COPPER.

	Found.	Per cent.	Calculated.
Copper	59·24	.....	59·45
Chlorine	16·87	.....	16·64
Oxygen	11·15	.....	11·25
Water estimated by difference	12·74	.....	12·66
	100·00		100·00

These numbers lead to the formula—

$$CuCl,3CuO,3HO \quad [CuCl^2,3CuO,3H^2O].$$

PROXIMATE COMPOSITION OF OXYCHLORIDE OF COPPER.

	Found.	Per cent.	Calculated.
Chloride of copper (cupric chloride)	31·93	.....	31·50
Protoxide of copper (cupric or black oxide)	55·33	.....	55·84
Water	12·74	.....	12·66
	100·00		100·00

Assuming that no hydrogen is evolved, the preceding reaction may be expressed by the following equation :—

$$4Cu+HCl+4O+2HO = (CuCl,3CuO,3HO).$$
$$[4Cu+2HCl+4O+2H^2O = (CuCl^2,3CuO,3H^2O).]$$

As it seemed to me important to ascertain what might be the effect of higher than atmospheric temperatures on some of the preceding reactions, I had the following experiments, Nos. 8 to 12, made in my laboratory by E. Jackson (1875): in each experiment the chloride of copper used was the ordinary crystallized salt; the water was replaced as it evaporated; but the solution, which was kept at or close to the boiling-point, was never much diluted. It should be stated, that the experiments were made chiefly for the purpose of determining the conditions most favourable for the conversion of sulphide of silver into chloride, by the action of chloride of copper; and that the numerical results must be regarded as merely approximate.

8. *Sulphide of silver, chloride of copper (cupric chloride), water, and heat.*—Sulphide of silver was boiled in a glass flask during 5 hours with an aqueous solution of chloride of copper, when it was found that 75% of the sulphide had been changed into chloride of silver.

9. *Sulphide of silver, chloride of copper (cupric chloride), air, water, and heat.*—The apparatus used was a flat-bottomed glass flask closed with a cork, through which descended nearly to the bottom a glass tube open at the top, but at the lower end closed and expanded into a small bulb pierced with numerous small holes. There also passed through the cork a short piece of glass tube, which was connected with the mouth of a vessel filled with water, such as is commonly employed for producing a current of air by aspiration. Into the

flask were put 81 grains of sulphide of silver, prepared by precipitation with sulphuretted hydrogen, and an aqueous solution of chloride of copper containing about 112 grains of the crystallized salt. The aspirating apparatus was set in action and a small Bunsen burner placed under the flask. The experiment was continued during about 8 hours. What was originally sulphide of silver had now become white, and a whitish powder had also been precipitated. The contents of the flask were transferred to a filter, and the substance which did not pass through was washed first with water and then with ammonia-water, which became deep blue, black sulphide of silver remaining on the filter. The ammoniacal solution was treated with nitric acid in excess, which caused a bulky precipitate of white chloride of silver, the weight of which was ascertained. The residue of black sulphide of silver was digested with nitric acid, and the silver which it contained was estimated as chloride. The results are as follow :—

	Grains.
Sulphide of silver operated upon	81·00
Sulphide of silver changed into chloride	68·08
do. remaining unchanged	12·82
	80·90

10. The apparatus used in the last experiment was not considered to be so effective as desirable, because much of the sulphide of silver sank down on the flat bottom of the flask and was not well stirred up. Accordingly, in the following experiment, a tube tapered nearly to a point at the bottom was substituted for a flask, and the lower end of the air-delivery tube was also drawn out fine, and the opening at this end made nearly to touch the bottom of the main tube. In other respects the arrangements were the same as in the last experiment. The quantities operated upon were 20 grains of sulphide of silver and 300 grains of crystallized chloride of copper dissolved in water. The experiment was continued during 8 hours. The contents of the tube were similar in appearance to those in the flask above described. The deposit was analysed, with the following results :—

			Grains.
Chloride of silver.....	Silver.....	12·26	16·29
	Chlorine	4·03	
Dichloride of copper*	Copper	5·56	8·82
	Chlorine	3·26	
Sulphide of silver			5·43
			30·54

* The chlorine and copper are not in the exact proportions required to form dichloride of copper, 5·56 grains of copper requiring only 3·105 grains of chlorine.

Thus, of the 20 grains of sulphide of silver operated upon it was found that 72% had been changed into chloride. However, a minute quantity of chloride of silver was, doubtless, dissolved in the residual solution of cupric chloride and not estimated.

Free sulphur was also found, but its weight was not determined : sulphuric acid may also have been produced.

The copper and chlorine, exclusive of that in the chloride of silver formed, are very nearly in the same ratio as in dichloride of copper (cuprous chloride).

The formation of the dichloride of copper is shown in the following equation :—

$$2CuCl + AgS = Cu^2Cl + AgCl + S.$$
$$[2CuCl^2 + Ag^2S = Cu^2Cl^2 + 2AgCl + S.]$$

It was not clearly ascertained whether any oxychloride of copper was simultaneously produced ; but it could, certainly, not have been formed in sensible quantity, as, in that case, the deposit would have had a green colour.

Now, if the whole of the dichloride of copper, resulting from the reaction shown in the preceding equation, had been present in the deposit along with the chloride of silver, it would have amounted to 11·66 grains, whereas only 8·82 grains were present. This deficiency may be explained by the fact that as dichloride of copper dissolves, to a certain extent, in a solution of chloride of copper, a portion of it doubtless was dissolved by the residual solution of that chloride.[1] As hardly any information on this point is to be met with in chemical treatises, even the most modern, the following experiment was made. To a concentrated solution of neutral chloride of copper (cupric chloride) crystals of dichloride of copper (cuprous chloride) were added, and on the application of a gentle heat were found immediately to dissolve and to impart a deep brown colour to the solution. The crystals remained dissolved in the solution when it had become cold.

11. The following experiment was made in the same apparatus as used in the last. The quantities operated upon were 18 grains of sulphide of silver and about 170 grains of crystallized chloride of copper (cupric chloride) dissolved in water. The heating of the tube was continued daily for several hours during a week, a current of air passing through all the while. The contents of the tube after this treatment were similar in appearance to those in the last experiment. The deposit was analysed, with the following results :—

	Grains.
Chloride of silver	19·64
Sulphide of silver	0·89
Copper	3·41
Chlorine	1·34
Sulphur (in a free state)	1·74
	27·02

Hence, 95·01% of the sulphide of silver operated upon had been

[1] On the solubility of cuprous chloride in a solution of cupric chloride, see Recherches sur l'Association de l'Argent aux Minéraux Métalliques, etc. Par MM. Malaguti et Durocher. Paris, 1850. p. 352.

changed into chloride. A small quantity of sulphur, 0·45 gr., in the state of sulphuric acid, was found in the chloride of copper solution after the experiment.

In this case, as the quantity of chlorine in the deposit (exclusive of that existing in the chloride of silver) was insufficient to form dichloride with the 3·41 grains of copper present (for which 1·905 grain would be required instead of only 1·34 grain), it is probable that oxychloride of copper was formed in sensible quantity. This would explain the excess of copper, as the proportion of copper to chlorine is much greater in oxychloride than in dichloride of copper.

As the present experiment was continued much longer than the last, a larger quantity of dichloride of copper would be dissolved, and there would be a larger proportion of chlorine to copper in the deposit.

12. *Sulphide of silver, dichloride of copper (cuprous chloride), air, water, and heat.*—This experiment was made in the same apparatus as used in the last two experiments. The quantity of sulphide of silver operated upon was 10 grains, and there was a considerable excess of the dichloride of copper and water. The experiment was continued at intervals during several days, for about 24 hours altogether. After air had passed through the apparatus for some time, the dichloride of copper became bright-yellow, then orange-red, and finally light-green. Only 0·11 gr. of sulphide of silver was found to have been changed into chloride. The quantity of sulphide of silver remaining unchanged was directly estimated and found to amount to 9·89 grs. A little sulphur had been converted into sulphuric acid, but how much was not ascertained.

There can be little doubt that the reason why so small a proportion of the sulphide of silver was decomposed is that the action was much retarded owing to both the sulphide of silver and dichloride of copper being in the solid state: it will be remembered that in the preceding experiments the chloride of copper was in solution.

Remarks.—An ammoniacal solution of dichloride of copper (cuprous chloride) has, according to Karsten, no action on sulphide of silver; but an aqueous solution of common salt containing the dichloride dissolved does exert an action, forming chloride of silver.[2]

13. *Sulphide of silver, sulphate of protoxide of copper (cupric sulphate), chloride of sodium, air, and water.*—Moist sulphide of silver was mixed with these salts. On adding chloride of sodium to an aqueous solution of sulphate of copper, the colour changes from blue to green, similar to that of chloride of copper when not too dilute, decomposition occurring, with the formation of sulphate of soda and chloride of copper.[3] When the examination took place, the liquid had the

[2] Op. antea cit.

[3] Boussingault adduced the following experimental results in proof of such decomposition. He triturated sulphate of copper and chloride of sodium together, and found that the mixture acquired an intense apple-green colour, and rapidly deliquesced. After several days the mixture was dried in the sun and then treated with alcohol, which immediately dissolved out sufficient chloride of copper to become deep-green; sulphate of copper, it will be remembered, is insoluble in alcohol. Ann. de Chim. et de Phys. 1832. 51. p. 354.

colour of a green aqueous solution of chloride of copper, and there was the same kind of light greenish deposit as in the preceding experiments, containing particles of undecomposed sulphide of silver diffused. The mixture was filtered. The filtrate yielded a *precipitate of chloride of silver*, and the residue contained *free sulphur*.

14. *Sulphide of silver, basic sulphate of sesquioxide of iron (basic ferric sulphate), chloride of sodium, and water.*—The salt of iron was prepared by evaporating sulphate of protoxide of iron (ferrous sulphate) with nitric acid, and washing with water in order to separate any remaining nitric acid. It was mixed with chloride of sodium and moist sulphide of silver. When examined, the mixture was filtered. The filtrate contained *chloride of silver*, which was precipitated on neutralizing with nitric acid.

Remarks.—Ferric sulphate has, it is stated, been successfully used as a substitute for cupric sulphate in the Mexican amalgamation process.[4]

According to Malaguti and Durocher, sulphide of silver is not acted upon by ferric sulphate alone.[5]

15. *Sulphide of silver, sulphate of protoxide of iron (ferrous sulphate), chloride of sodium, and air.*—Moist sulphide of silver was mixed with these two salts. When examined, the liquid was decanted, and ammonia-water poured on the residue. The ammoniacal solution was filtered, and neutralized with nitric acid, when it yielded *a precipitate of chloride of silver*. The residue insoluble in ammonia was digested with warm hydrochloric acid (consisting of $\frac{1}{3}$ by measure of concentrated acid and $\frac{2}{3}$ of water), in order to dissolve the basic sulphate of sesquioxide of iron (basic ferric sulphate) which had been formed. The insoluble residue was washed with ammonia-water, to ensure the removal of all traces of chloride of silver, after which it was digested with an aqueous solution of potash. This solution, it was proved in the manner previously described, had dissolved *free sulphur*.

16. *Sulphide of silver, sulphate of protoxide of iron, and chloride of sodium, without access of atmospheric air.*—Another experiment was made in which access of atmospheric air was prevented. Sulphide of silver and chloride of sodium were added to a saturated aqueous solution of sulphate of protoxide of iron (ferrous sulphate) contained in a bottle, which was then closely stoppered, so as to exclude air. It contained *no chloride of silver*. Atmospheric oxygen is, therefore, essential to the formation of chloride of silver under the conditions in the last experiment.

Conclusions from the foregoing Experiments.—The following conclusions from the preceding experiments, made in my laboratory, appear to be warranted :—

I. When sulphide of silver is exposed to the action of chloride of sodium, air, and water at ordinary temperatures, *no chloride of silver* is formed.

[4] Notice sur le Traitement de l'Argent, à Tetela del Oro, au Mexique; par M. Jules Guillemin. Bulletin de la Soc. de l'Industrie Minérale, 1856-7. 2. p. 310.

[5] Op. cit. p. 253.

II. When sulphide of silver is exposed to the action of chloride of copper, air, and water, at ordinary temperatures, chloride of silver and oxychloride of copper are formed, with the separation of free sulphur and the production of a small quantity of sulphuric acid. These changes appear to be the result of two reactions: one primary, which is represented in the following equation:—

$$AgS + 2CuCl = AgCl + Cu^2Cl + S$$
$$[Ag^2S + 2CuCl^2 = 2AgCl + Cu^2Cl^2 + S];$$

the other secondary, which is represented in the following equation:—

$$AgS + 2Cu^2Cl + 3O + 3HO = AgCl + (CuCl,3CuO,3HO) + S.$$
$$[Ag^2S + 2Cu^2Cl^2 + 3O + 3H^2O = 2AgCl + (CuCl^2,3CuO,3H^2O) + S.]$$

From these two reactions it will be seen that with a given weight of chloride of copper twice as much sulphide of silver is decomposed by the first reaction as by the second.

III. When sulphide of silver is boiled with a concentrated aqueous solution of chloride of copper in excess, chloride of silver is rapidly formed.

IV. When sulphide of silver is exposed to the action of a boiling concentrated aqueous solution of chloride of copper, through which air is kept passing, chloride of silver is rapidly formed; but probably not more rapidly than without air: sulphur being set free, and sulphuric acid produced in small quantity.

V. When sulphide of silver is boiled with dichloride of copper in water through which a current of air is kept passing, only a very small quantity of chloride of silver is formed. This may probably be explained by the insolubility of both substances in water; and it may be safely inferred that no greater action would have taken place at ordinary temperatures.

VI. When sulphide of silver is exposed to the action of chloride of copper, chloride of sodium, air, and water at ordinary temperatures, chloride of silver is formed and sulphur set free.

VII. The same reaction as in the last case takes place when dichloride of copper is substituted for the chloride. The efficacy of the dichloride in this case is probably due to its solubility in chloride of sodium, whereby its contact with the sulphide of silver must be greatly increased.

VIII. The same effect is produced when sulphate of protoxide of copper is substituted for the chloride, in the presence of chloride of sodium, air, and water. Chloride of copper and sulphate of soda are first produced, and then the chloride of copper acts upon the sulphide of silver as in the previous cases.

IX. When sulphide of silver is exposed to the action of sulphate of sesquioxide of iron, chloride of sodium, and water, at ordinary temperatures, chloride of silver is produced.

To obtain this result it is not essential that air should be present. But, if sulphate of protoxide of iron be substituted for the basic sulphate of sesquioxide, chloride of silver is not produced without

the presence of air. This indicates that a salt of sesquioxide of iron must be formed before the sulphide of silver is decomposed. But further investigation is needed in order satisfactorily to explain the reaction.

Sulphide of silver, heated with chloride of sodium, chloride of magnesium, or iron-pyrites and steam.—Moesta has investigated this subject, and obtained the following results.

When sulphide of silver, in admixture with chloride of sodium, is subjected to the action of steam, chloride of silver is formed. This formation, however, of chloride of silver by steam at 100° C. takes place very slowly, and is hardly to be detected if chloride of sodium alone is used; but, on the contrary, when chloride of magnesium is also present, the reaction is very decided. At a higher temperature the change takes place much more quickly. The formation of chloride of silver is hastened by the addition of finely-powdered iron-pyrites to the sulphide of silver, which Moesta ascribes to the facility with which the sulphur of the pyrites is, under the circumstances, converted into sulphuric acid.[6]

Sulphide of silver and antimony (pyrargyrite), and sulphide of silver and arsenic (proustite), with chloride of copper and water.—The composition of these substances will be found stated in the sequel in the article on the Ores of Silver. According to Malaguti and Durocher, when pyrargyrite is exposed to the action of an aqueous solution of chloride of copper, changes take place similar to those above recorded in the case of sulphide of silver alone. If there be access of air, they state that "sulphuric acid and a mixed deposit of chloride of silver and oxychloride of copper are formed; and that the antimony passes into the solution, from which it is precipitated along with the copper by a plate of zinc: by the action of nitric acid on this precipitate antimonic acid is left."[7]

They have experimented on this subject and obtained the following results. Flasks of equal capacity were used, and simultaneously shaken from time to time. In each experiment the quantity of the double sulphide operated upon contained 0·100 gramme of metallic silver, which corresponds to 0·133 gramme of chloride of silver; and the quantity of solution employed was 30 cubic centimetres, which contained 0·30 gramme of cupric chloride:—

	Weight of the substance in grammes.	Duration of experiment.	Chloride of silver produced. In milligrammes, cupric chloride solution.	With the addition of 0·272 gram. of chloride of sodium.	With the addition of 5 gram. of cupric sulphate and 2·5 of chloride of sodium.
Pyrargyrite	0·166	2 months	69	63	63
Proustite	0·140	3 „	14	—	—

Hence it appears that cupric chloride attacked pyrargyrite much more energetically than proustite; and that while the presence of

[6] Ueber das Vorkommen der Chlor-, Brom- und Iodverbindungen des Silbers in der Natur, pp. 40, 41.

[7] Op. cit. p. 249.

chloride of sodium did not promote the formation of chloride of silver, as it does in the case of the simple sulphide of silver, it completely checked it in the case of proustite.[8] It would not be safe to accept these results without additional confirmation by experiment.

Argentiferous galena, chloride of copper, air, and water.—Malaguti and Durocher have recorded the following experiment upon this subject. They exposed a galena from Freiberg, which contained 3·11% of silver, to the action of an aqueous solution of chloride of copper and air, during four months, and investigated what occurred at three different times during that period. They state that oxychloride of copper, chloride of lead, and sulphate of copper were produced, and that the chloride of lead dissolved slowly in the liquor, when sulphate of lead was formed and chloride of copper reproduced. After the lapse of three months there was no chloride of silver, though most of the galena had then been decomposed; and it was not until three months and a half had expired, that any chloride of silver was found.[9]

Argentiferous blende, chloride of copper, air, and water.—An experiment similar to that last described was also made by the same chemists upon blende (sulphide of zinc), which contained 0·2% of silver, and in which they obtained evidence for concluding that the silver existed as sulphide, in intimate mixture, if not in actual combination, with the sulphide of zinc. After the lapse of eight months, a notable quantity of the blende had been decomposed, and zinc had passed into the solution; sulphuric acid and oxychloride of copper were formed, but not the slightest trace of chloride of silver could be detected. The absence of chloride of silver, under the circumstances, is not, they remark, surprising; because they ascertained that the blende operated upon could decompose a little more than 5% of chloride of silver, and, consequently, when this blende is subjected to the action of chloride of copper, the formation of chloride of silver could not begin to take place until nearly the whole of the blende had been decomposed, and the remainder contained about 3·8% of silver.[1]

Argentiferous iron-pyrites or copper-pyrites, chloride of copper, air, and water.—Malaguti and Durocher ascertained that the reactions are similar to those in the preceding experiments with galena and blende; there is always chlorination of the metal, formation of sulphuric acid, and precipitation of oxychloride of copper; chloride of silver being produced only late in the course of the experiment.[2]

FORMATION OF CHLORIDE OF SILVER FROM SULPHATE OF SILVER.

Chloride of silver is formed when hydrochloric acid or chloride of sodium is added to a solution of sulphate of silver in water, or in water acidulated with sulphuric acid. It is also produced when a mixture of sulphate of silver and chloride of sodium is heated to dull redness; and this reaction takes place in Augustin's process for the extraction

[8] Op. cit. p. 417. [9] Op. cit. p. 249. [1] Op. cit. p. 250. [2] Op. cit. p. 251.

of silver from argentiferous regulus of copper or iron. The decomposition is shown in the equation :—

$$AgO,SO^3+NaCl=AgCl+NaO,SO^3.$$
$$[Ag^2SO^4+2NaCl=2AgCl+Na^2SO^4.]$$

The following experiment on this mode of formation of chloride of silver has been made in my laboratory by H. Louis (1876) :—A mixture of 104 grains of sulphate of silver and 39 grains of chloride of sodium was kept molten during 15 minutes, and the mass allowed to cool in the crucible. When cold, it was found to consist of two layers. The upper layer had a faint pink hue, darkening somewhat on exposure to light; it was opaque and stone-like, and consisted mainly of sulphate of soda. The lower layer was at first yellow, and darkened rapidly on exposure to light; it was crystalline, sectile, and horny, and consisted almost entirely of chloride of silver, as it lost only 0·026 grain (0·35%) by boiling in water acidulated with a few drops of sulphuric acid.

MODES OF REDUCTION OF CHLORIDE OF SILVER.

By hydrogen.—When chloride of silver is heated to or beyond its melting-point in a current of hydrogen, it is completely reduced with the evolution of hydrochloric acid : thus,

$$AgCl+H=Ag+HCl \quad [\text{idem}].$$

The following experiment on this subject has been made in my laboratory by E. Jackson (1875). A U-tube containing chloride of silver was immersed in an oil-bath, of which the temperature was gradually raised, hydrogen passing through the tube all the while. The gas on leaving the tube was tested constantly for hydrochloric acid, by holding in it a glass rod moistened with ammonia-water; but not until the temperature reached 260°C., which is stated to be the melting-point of chloride of silver, was there any appearance of the white fume of chloride of ammonium, though Rodwell, as previously stated,[3] has recently announced that there is reason to believe that the melting-point of chloride of silver is near 360° C.

Chloride of silver, it may be here stated, is *not reduced* when heated in a current of steam, at least at any temperature below or up to 260° C., as has been proved by experiment in my laboratory by E. Jackson (1875). A weighed quantity of chloride of silver was heated for 1½ hour in a glass tube, through which a current of steam was kept passing all the while. The steam, after leaving the tube, was conducted into a U-tube containing water. The weight of the chloride of silver was found to be the same after the experiment as it was before, and not a trace of hydrochloric acid was detected in the water condensed in the U-tube. In another experiment, of longer duration, the chloride of silver became fused towards the end of it, but without the slightest evidence of decomposition.

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[3] P. 57 *antea*.

By potash.—Professor Gregory suggested the following method for the preparation of pure silver from chloride of silver, but only when the latter has been freshly precipitated and is still moist. The precipitated chloride is to be broken down during washing, but not ground in a mortar, which causes it to cake and so impedes the action of the potash. In this state it is to be boiled with a solution of caustic potash, having a specific gravity of 1·25 *at least;* and during the boiling it is to be well stirred in order to bruise all curdy or lumpy particles. In five or ten minutes it will become black, when a small portion should be taken out, washed and digested with nitric acid. If it does not entirely dissolve, the solution of potash must be decanted, the powder, while still moist, well ground in a mortar (which may now be done with advantage) and again boiled with fresh solution of potash for five minutes. After this treatment it should be wholly soluble in nitric acid; but if not, a second grinding and boiling "will infallibly succeed." Oxide of silver is thus produced, which is described as very dense, homogeneous, and pure black, with, if anything, a tint of blue. By heating the oxide sufficiently, pure silver is obtained. The action of the potash is thus shown—

$$AgCl + KO = AgO + KCl.$$
$$[2AgCl + K^2O = Ag^2O + 2KCl.]$$

It is particularly to be noticed, that when the chloride of silver has once been dried, it is with great difficulty decomposed, even by long boiling with potash.[3] According to H. Rose, a solution of potash decomposes chloride of silver only when heated.[4]

By heating with an aqueous solution of caustic potash or soda and various organic substances, such as sugar (cane or grape), honey, and sugar of milk, or with carbonate of soda and grape-sugar.—Metallic silver in the state of powder is thus directly obtained; but this method has, so far as I am aware, been rarely adopted by practical metallurgists. R. Böttger, however, recommends a process of this kind as the best for reducing not only chloride of silver, but all the salts of silver, whether soluble or insoluble in water; and gives the following directions for conducting it:—Chloride of silver is to be boiled with its own weight of starch-sugar (*i.e.* grape-sugar or glucose), and a solution of carbonate of soda, consisting of 1 part of the crystallized salt and 3 parts of water; when, in less than a few minutes, the whole of the silver will be reduced to the metallic state.[5] Pelouse states that reduction of chloride of silver by boiling with a solution of caustic potash and sugar had been practised by Levol at the Paris Mint before Böttger published his process.[6] Numerous interesting observations on the reduction of chloride of silver by organic substances have been made by H. Vogel and others.[7] Reduction of the chloride by zinc, which has been previously men-

[3] Philosophical Magazine, 1843. 22. p. 283.
[4] Chemical Gazette, 1847. 5. p. 2.
[5] Jahresber. 1855. p. 418.
[6] Idem, 1851. p. 368.
[7] Idem, 1862. pp. 223-227.

ioned, is so certain, simple, inexpensive, and convenient, that in ny opinion it leaves nothing to be desired, provided it be skilfully conducted. I have tried most of the methods of reduction proposed with a view to operations on the large scale, and my experience has led me to prefer this method to all others. I do not, therefore, consider it necessary to enter into further details concerning the modes of reduction last mentioned.

By carbonate of soda or potash.—When a mixture of chloride of silver and either of these carbonates is cautiously heated to the melting-point of silver, the chloride is completely reduced, thus :—

$$AgCl+NaO,CO^2=Ag+NaCl+O+CO^2.$$
$$[2AgCl+Na^2O,CO^2=2Ag+2NaCl+O+CO^2.]$$

It need hardly be remarked that it is desirable there should be a large excess of carbonate, twice the weight of the chloride at least ; but even in that case, as the chloride of silver melts before decomposing, some of it may find its way to the sides of the earthen crucible, in which the experiment may be made, and so escape by permeation. The crucible should be large enough to hold about twice the bulk of the mixture operated upon. The heat should be gradually raised to the melting-point of silver. Aikin states that whatever care is taken in the reduction, it is seldom that quite 75 parts of silver can be obtained from 100 parts of chloride,[8] but that is the theoretical proportion in pure chloride. In this process much will depend on proper regulation of temperature. Various precautions have been suggested with a view to lessen the risk of loss by permeation or projection, but none seem entirely satisfactory. Thus it has been recommended to melt the alkaline carbonate and drop in the perfectly dry chloride in successive small portions. A mixture of the two carbonates of potash and soda has been proposed, as the melting-point of such a mixture is lower than that of each separately.

Hydrate of potash or soda acts like the carbonate of either of these alkalies, thus :—

$$AgCl+KO=Ag+KCl+O.$$
$$[2AgCl+K^2O=2Ag+2KCl+O.]$$

According to Berthier, chloride of silver is decomposed in the *wet* as well as in the *dry* way by these alkaline carbonates.[9] Berzelius, on the contrary, asserts that in the *wet* way, the alkaline carbonates have no action upon it.[1] H. Rose states that solutions of the alkaline carbonates do not decompose chloride of silver in the cold, and only to a very slight extent on the application of heat.[2]

By NaO,SO $[Na^2SO^2]$.—According to G. Scutari, when freshly-precipitated chloride of silver is heated with freshly-prepared so-called hydrosulphite of soda (*Natriumhydrosulfit*),[3] metallic silver is

[8] Chemical Dictionary, 2. p. 319.
[9] Tr. des Ess. 2. p. 790.
[1] Tr. de Chim. 4. p. 262.
[2] Chem. Gaz. 1847. 5. p. 2.

[3] This is the sodium salt of a new acid discovered by Schützenberger, of which an account has been given in a note on p. 49.

produced with the evolution of sulphurous acid: this reaction is explained by the following equation:[4]—

$$NaO,SO + AgCl = Ag + NaCl + SO^2.$$
$$[Na^2SO^2 + 2AgCl = 2Ag + 2NaCl + SO^2.]$$

Another salt of the same acid, containing only half the quantity of sodium, has been described, in which case the reaction is:—

$$NaO,HO,2SO + 2AgCl = 2Ag + NaCl + HCl + 2SO^2.$$
$$[NaHSO^2 + 2AgCl = 2Ag + NaCl + HCl + SO^2.]$$

By lime and carbon.—Chloride of silver is reduced when heated, say to the melting-point of silver, in admixture with these substances in suitable proportions. Gay-Lussac recommended the following proportions: an intimate mixture of 100 parts by weight of chloride of silver, 20 of dry lime, and 4·2 of charcoal is to be gradually raised to the melting-point of silver. Effervescence occurs and the reaction is as under:—

$$2AgCl + 2CaO + C = 2Ag + 2CaCl + CO^2.$$
$$[4AgCl + 2CaO + C = 4Ag + 2CaCl^2 + CO^2.]$$

It has been stated that great loss occurs with these proportions.[5]

By carbonate of lime.—According to Malaguti and Durocher, when chloride of silver is heated with carbonate of lime, it is reduced to the metallic state.[6] It has been asserted that in the wet way carbonate of lime decomposes chloride of silver; but Malaguti and Durocher found that when water containing the latter and very finely divided chalk was boiled, hardly sensible traces of chloride of calcium were formed. They tried also the effect of caustic lime, in admixture with chloride of sodium, siliceous sand, and water, upon chloride of silver at ordinary temperatures, and found that after the lapse of 4 days, during which the mixture had been frequently agitated, there was no appreciable action.[7] When chloride of calcium and carbonate of silver are placed in contact with water for a few moments, double decomposition promptly occurs.[8]

By dichloride of copper (cuprous chloride). Cu^2Cl [Cu^2Cl^2].—When ammoniacal aqueous solutions of dichloride of copper and chloride of silver are mixed in suitable proportions, the whole of the silver is immediately precipitated in the metallic state with the formation of chloride of copper, thus:—

$$AgCl + Cu^2Cl = Ag + 2CuCl.$$
$$[2AgCl + Cu^2Cl^2 = 2Ag + 2CuCl^2.]$$

The result is the same when only one of these substances is in solution, and when a solution of one in ammonia-water is added to the other dissolved in a concentrated solution of chloride of sodium;

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[4] Wagner's Jahres-Ber. 1875. p. 616.
[5] Gmelin's Handbook, 6. p. 136.
[6] Op. cit. p. 368.
[7] Op. cit. p. 474.
[8] Op. cit. p. 364.

ut when both are dissolved in solutions of this salt and then mixed, here is as little action as with pure water.[9] We have confirmed the accuracy of this and the preceding statements. We find that not the slightest reduction of silver occurs on the addition of cuprous chloride, dissolved in an aqueous solution of chloride of sodium, to a saturated solution, even boiling, of chloride of silver in a saturated solution of chloride of sodium. According to Millon and Commaille, 1 litre of ammonia-water, of the sp. gr. 0·924, dissolves 58 grammes of silver in the state of chloride; and for the complete reduction and precipitation of the silver from such a solution 230 cubic centimetres of a completely-saturated ammoniacal solution of dichloride of copper are required.[1]

According to Malaguti and Durocher, cuprous chloride, especially when it has not been melted, very easily reduces, at the ordinary temperature, chloride of silver to subchloride, with the formation at the same time of cupric chloride and a greenish-yellow substance, which dissolves in ammonia-water and communicates to it an intense blue colour. This latter product they regarded as an oxychloride, resulting from the action of the air upon that portion of the cuprous chloride which had become soluble in the nascent cupric chloride. This reaction, they state, may be shown by putting cuprous chloride, chloride of silver, and water into a flask; then, after the lapse of a few minutes, decanting the liquid, pouring ammonia-water upon the residue, washing with ammoniacal water until it ceases to become blue, and finally with pure water: there is thus obtained a greyish insoluble residue of very finely divided metallic silver. It was this state of extreme division of the silver which led Malaguti and Durocher to think that the chloride of silver had been reduced to subchloride and not to the state of metallic silver; for, they continue, if it had been completely reduced, there would be no reason why the resulting metal should be very finely divided, and such as it ought to be when it is separated from a solution. On the other hand, it is known that subchloride of silver is decomposed by contact with ammonia into normal chloride and into perfectly pulverulent metallic silver.[2]

As this is a subject of much scientific interest, I have presented *in extenso* the evidence adduced by Malaguti and Durocher in support of their view, that subchloride of silver is formed by the action of cuprous chloride on chloride of silver; evidence which appears to me to be far from conclusive. It has been previously shown that metallic silver reduces cupric chloride, when dissolved in water, to cuprous chloride, with the formation of chloride of silver. But now it appears that cuprous chloride reduces chloride of silver, with the separation of metallic silver! It will probably be found that an aqueous solution of cupric chloride, containing a certain proportion of cuprous chloride, has no action either on metallic silver or chloride of silver.

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[9] Karsten, Archiv, 2. ser. 25. p. 183.

[1] Jahresber. 1863. p. 284.

[2] Op. cit. p. 375.

By dioxide of copper (cuprous oxide) and either alum, ferrous or cupric sulphate.—Malaguti and Durocher found that cuprous oxide had no appreciable action upon chloride of silver, even at 100° C.; but that in the presence of a solution of either alum, ferrous sulphate, or sulphate of copper, considerable reduction took place.[3] (See p. 108.)

By protochloride of tin (stannous chloride).—According to H. Rose, "a solution of stannous chloride, to which sufficient hydrochloric acid has been added to render it clear, produces a white precipitate of chloride of silver, when it is added in small quantity to a silver-oxide solution [*i.e.* a solution of a silver salt.] But when a larger quantity of stannous chloride is added, the silver is reduced and precipitated as a brown-black powder, of only small bulk."[4] We have found that by adding first a few drops of a solution of nitrate of silver to a large quantity of cold water, then a little hydrochloric acid in excess of what was required to convert the silver into chloride, and lastly a few drops of an aqueous solution of stannous chloride, the colour of the milky liquid was not changed; but on subsequently heating this liquid, a dark brown precipitate was formed in it. In similar experiments, in which the addition of hydrochloric acid was omitted, the liquid immediately acquired a fine brown coloration without becoming sensibly turbid; but when larger proportions of the two substances were used, the liquor became immediately very dark brown and opaque, and a precipitate of the same colour was formed. This precipitate was found to be insoluble in ammonia-water, but to dissolve in nitric acid, thus indicating the probability that it was metallic silver. The colour of the clear liquor in the first experiment was of a rich yellowish-brown, not unlike the tint in some kinds of glass stained by silver. Possibly the silver-stain of glass may be due to metallic silver in an extremely fine state of division, just as the colour of the liquor above mentioned seems to have been due to that cause. In support of this view may be adduced the ruby colour of glass, which Faraday clearly proved to be due to gold in an extremely fine state of division.

By colophony.—Chloride of silver is reduced to the metallic state when heated with this substance, which is commonly called "rosin." I have tried it upon some quantity of chloride, and never wish to repeat the experiment; for a worse process on the score of inconvenience could not well be devised. Gmelin gives the following directions for conducting this process:—A crucible is to be filled nearly to the top with a mixture of 3 parts of chloride of silver and 1 part of colophony, and then gently heated, when the resin burns with a green flame, owing to the hydrochloric acid generated from the chlorine of the chloride and the hydrogen of the resin. The heat is afterwards raised so as to melt the silver, a little borax having been added. The crucible is to be tapped gently once or twice to facilitate the union of the silver. It is stated that the

[3] Op. cit. p. 388.
[4] Ausführliches Handbuch der analytischen Chemie, 1851. 1. p. 172.

process was first proposed by E. Mohr.[5] In the same way also is explained the partial reduction that occurs when, in analysis, chloride of silver is incinerated along with a filter.

By charcoal.—Wittstein, after having tried various methods of reducing chloride of silver, recommends that by charcoal as "the most simple, surest, and cheapest of all," and gives the following directions for practising it:[6]—A carefully made mixture of 2 parts of chloride of silver and 1 part of moist charcoal-powder is to be pressed into a plumbago crucible, which, having a piece of tile laid over its mouth, is then heated, and kept hot for a quarter or half an hour after hydrochloric acid gas has ceased to be evolved, after which the temperature is raised so as to melt the silver. Reduction is ascribed wholly to the hydrogen in the charcoal; for no chlorine is given off in the operation, but only hydrochloric acid. No reduction occurs when pure carbon is substituted for charcoal.

By various Metals.—*By zinc.*—Chloride of silver is reduced in the *dry* way by zinc. The reduction of chloride of silver by zinc in the *wet* way has previously been referred to. On the large scale the zinc may be most conveniently used in the form of bars. I have found bars about 1 in. square and 1 ft. long suitable for the purpose. The precipitated chloride is to be washed with water and put into water acidulated with hydrochloric acid. The zinc bars are then introduced, and it is desirable that the quantity of zinc should greatly exceed what is theoretically required, as in that case, after complete reduction of the chloride of silver, the residual zinc is in sufficiently large pieces to admit of being easily removed. Effervescence occurs, which is due to the evolution of hydrogen. Reduction is much promoted by heat, which may easily be applied by means of high-pressure steam, say 25 lbs. to the inch, through an earthenware or copper pipe descending to a considerable depth below the surface of the liquid. Large jars of Vauxhall stoneware holding from 60 to 90 gallons are well adapted for reduction in this way. They are to be set in cylindrical jackets of wrought-iron, say about 4 in. wider within than the jars are without, and the intervening space is to be filled with a mixture of sand and molten sulphur. Such vessels, when properly arranged, last a long time, even after they may have been cracked by the concussive effect of the steam. This kind of earthenware resists the long-continued action of boiling hydrochloric or nitric acid. The deposited silver is to be tested for intermixed chloride, and this is best done by heating a little of it with somewhat dilute nitric acid, in which it should wholly dissolve. If an insoluble residue remains, it is chloride of silver, and the reduction is not complete. The supernatant liquid is to be drawn off by means of a syphon, say of copper, and the deposit of silver is to be well washed with hot water, and then dried. The dry silver is to be moistened with an aqueous solution of nitrate of potash or soda, and again dried: the mixture of silver and nitrate when dry should contain about 5% of

[5] Chemical Gazette, 1845. 3. p. 77.

[6] Idem, 1849. 7. p. 354.

the latter. All that remains to be done is carefully to melt the mixture in large clay crucibles, adding small portions at a time, to skim the surface of the molten metal, and pour it into ingot-moulds. The metal will be brittle and must be re-melted; or, after skimming, the oxygen absorbed by the molten silver from the nitrate may be separated by stirring with a well-carbonized stick, whereby a tough ingot will be directly obtained.

Chloride of silver in contact with zinc under water is pretty quickly and completely reduced; and it is also reduced by *dry* contact with zinc in atmospheric air containing aqueous vapour.[7]

The whole of the silver is quickly precipitated by zinc from an ammoniacal solution of chloride of silver.[8]

Kuhlmann found that the liquid, in the midst of which hydrogen is evolved by the action of dilute sulphuric acid on zinc, does not reduce chloride of silver; and that a communication between the chloride and the zinc, either direct or by the medium of a conducting body, is essential for such reduction. But if the metallic salt be in solution, reduction proceeds rapidly.[9]

By iron.—Chloride of silver is reduced in the *dry* way by iron. Moist chloride of silver is reduced at ordinary temperatures by contact with iron; and the action is promoted by the presence of an aqueous solution of chloride of sodium, in which, it will be remembered, chloride of silver is somewhat soluble. This mode of reduction was adopted in the Freiberg amalgamation process for the extraction of silver from certain of its ores. The reaction is thus shown :—

$$AgCl + Fe = Ag + FeCl.$$
$$[2AgCl + Fe = 2Ag + FeCl^2.]$$

Reduction of chloride of silver by iron may be effected in the same manner as by zinc in the manner described. It is also reduced by contact with iron under water, or in atmospheric air containing aqueous vapour.[1] Iron precipitates silver with metallic lustre from a solution of chloride of silver in ammonia-water; but it does not act, or only very slightly, upon any chloride of silver remaining undissolved by the ammoniacal liquid.[2]

Malaguti and Durocher found that the addition of an aqueous solution of sulphate of iron or of alum produced "very favourable" results by considerably increasing the percentage of silver obtained in a given number of hours, when chloride of silver was exposed to the action of metallic iron.[3]

By copper.—Chloride of silver is reduced in the *dry* way by copper. When chloride of silver is dissolved in a strong aqueous solution of chloride of sodium, say at about 100° C., the whole of the silver may be

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[7] Fischer, Das Verhältniss der chemisch. Verwandtschaft zur galvanisch. Elektricität, 1830. pp. 116, 119.
[8] Idem, p. 118.
[9] Chemical Gazette, 1855. 13. p. 473. From the Compt. rendus, Oct. 8. 1855 p. 538.
[1] Fischer, op. cit. p. 116.
[2] Idem, p. 118.
[3] Ann. des Mines, 1850. 17. p. 382.

precipitated in the metallic state by the immersion of metallic copper; and this mode of reduction is adopted in the Augustin process for the extraction of silver from certain argentiferous metallurgical products. In contact with copper under water, chloride of silver is very slowly and imperfectly reduced.[4] Copper throws down all the silver in the metallic state from an ammoniacal solution of chloride of silver.

The following observations on the reduction of chloride of silver by copper are by Malaguti and Durocher:—Copper, even in the presence of an acid, reduces chloride of silver very slowly in the cold. This fact is the more striking because iron and zinc rapidly reduce it without the intervention of any acid. They found that when 0·1 gramme of fused chloride of silver was immersed in acidulated water, it was completely reduced by zinc in a quarter of an hour; whereas, under exactly the same conditions, only about half of that quantity had been reduced by copper after the lapse of 18 hours. Flocculent chloride of silver in water not acidulated was reduced by iron and zinc almost immediately with disengagement of heat, whilst copper gave only feeble signs of action after contact during several days. But it is otherwise at a high temperature: the same flocculent chloride of silver was reduced by copper with facility at 100° C.[5]

By lead.—Chloride of silver is reduced in the *dry* way by lead. It is also slowly reduced by contact with lead under water. Lead acts like iron upon a solution of chloride of silver in ammonia-water, and throws down the whole of the silver in the bright metallic state upon the sides of the vessel; but it is without action upon any chloride left undissolved by the ammoniacal solution.[6]

By mercury.—Chloride of silver is reduced by mercury at ordinary temperatures, with the formation of calomel, thus:—

$$AgCl + 2Hg = Ag + Hg^2Cl.$$
$$[2AgCl + 2Hg = 2Ag + Hg^2Cl^2.]$$

If the mercury is in excess, an amalgam of silver is obtained. This reaction occurs in the Mexican Amalgamation Process. According to Fischer, chloride of silver is very slowly and imperfectly reduced by contact with mercury under water.[7] Marggraf reduced chloride of silver by grinding it in a glass mortar with about twice its weight of dry carbonate of ammonia and just enough water to give it the consistency of soup, after which 6 times its weight of mercury were added and trituration was continued for some hours. The calomel formed was washed off with water from time to time. He found that when silver-amalgam was heated with calomel, chloride of silver was formed and mercury volatilized.[8]

According to the experiments of Malaguti and Durocher, the reduction of chloride of silver by mercury is much promoted by the presence of certain salts. Thus, after a paste formed of 10 grammes

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[4] Fischer, op. cit. p. 116.
[5] Op. cit. p. 384.
[6] Fischer, op. cit. p. 118.
[7] Op. cit. p. 116.
[8] Aikin's Dictionary, 2. p. 319.

of clay, 0·2 gramme of chloride of silver, 5 grammes of one of t undermentioned salts, and 19 grammes of mercury, had been kept movement during 24 hours in their rotating apparatus, the amou of silver extracted, stated in hundredths of the total quantity silver present, were as follow :—

Alum [potash alum?]	13·65
Ferrous sulphate	9·48
Cupric sulphate	6·73
Mercury alone	4·42

As the salts above named have no solvent action on chloride silver, Malaguti and Durocher suggest that possibly there may electric currents produced by the contact of the mercury with the fi portions of silver reduced, and that the solutions of these salts m act as conductors.[9]

The presence of an aqueous solution of chloride of sodium pr motes the reduction of chloride of silver by mercury, owing, it believed, to the solvent action of that solution upon chloride of silv The following experiments were made by Malaguti and Duroche They kept in agitation, during 50 hours, mixtures of 0·130 gram of chloride of silver (= 0·100 gramme of metallic silver)—which w sometimes dissolved in the saline solution, at other times suspended water—with always 50 grammes of washed sand, 150 cubic centimet of liquid, and 20 grammes of mercury. In some experiments on half the quantity of chloride of silver was operated upon. T results are as follow:—

State of the chloride of silver, containing in general 1000 of metallic silver.	Silver removed b the mercur expressed i thousandth
1. Dissolved in the saline solution	461
2. Do. do. with half the quantity of chloride of silver	75
3. Curdy, dried at 100° C., and suspended in water	153
4. Do. do. with half the quantity of chloride of silver	33
5. Crystallized, artificial chloride of silver, suspended in water	158
6. Chloride of silver slightly melted with sand and suspended in water	62
7. Native chloride of silver, with its matrix, suspended in water	Traces.

According to G. Campani, silver, especially when finely divide completely precipitates mercury at ordinary temperatures, in t course of a few hours, from a solution of chloride of mercu according to the following equation :[2]—

$$HgCl + Ag = AgCl + Hg.$$
$$[HgCl^2 + 2Ag = 2AgCl + Hg.]$$

A similar reaction is stated to occur in the case of iodide of mercu dissolved in iodide of potassium.

How this reaction is to be reconciled with the well-establish

[9] Op. cit. p. 369. [1] Op. cit. p. 372.
[2] Jahresber, 1870. p. 373.

fact that mercury reduces chloride of silver, with the formation of calomel and silver-amalgam, I am at a loss to conceive. I find, however, that on adding precipitated silver to an aqueous solution of chloride of mercury, especially when heated, there is an immediate action, and the formation of a fine, *grey* powder, which I examined under a microscope, without detecting the faintest trace of metallic globules. What this grey powder may be must be ascertained by further investigation.

By iron and mercury.—Malaguti and Durocher experimented upon the relative rapidity with which the reduction of chloride of silver is effected by iron, by mercury, and by these two metals together. They have presented their results in the following tabular form :—

TABLE SHOWING THE RELATIVE RAPIDITY OF REDUCTION OF CHLORIDE OF SILVER BY IRON, BY MERCURY, AND BY IRON AND MERCURY TOGETHER.

Description of matrix (apparently artificial).	Percentage of the total silver obtained by agitation with iron and mercury for 10 hours.	Percentage of the total silver obtained by agitation with mercury alone for 10 hours.	Percentage of the total silver obtained by ebullition with iron alone for 3 hours, followed by agitation with mercury alone for 10 hours.	Percentage of the total silver obtained by agitation with iron alone for 20 hours and with mercury alone for 10 hours.
Oxide of iron ...	96·9	12·6	90·3	43·1
Clay.....	92·9	8·5	84·0	28·6

They remark that these results indicate that the influence of the contact of the two metals is "very considerable," and they attribute the increase in the rapidity of reduction under these circumstances to galvanic action.

The same chemists state that they found the presence of ferrous sulphate or alum greatly to favour the combined action of iron and mercury on chloride of silver; insomuch that, with the intervention of these salts, the reducing action was, on the average, three quarters more than with iron alone.[3]

By certain other metals.—Chloride of silver is reduced in the *dry* way by tin, antimony, and bismuth. It is reduced at ordinary temperatures by tin, antimony, bismuth, and arsenic, but only when moistened with water: the action is more rapid when it is moistened with dilute hydrochloric acid, and much more rapid with an aqueous solution of chloride of sodium.[4] Fischer states that under water chloride of silver is reduced pretty quickly and completely by contact with cadmium, cobalt, and arsenic, slowly by nickel, very slowly and imperfectly by antimony, and most slowly of all by tin, bismuth, and manganese.[5] Bismuth has no action on chloride of

[3] Op. cit. p. 383.

[4] Berthier, Tr. des Ess. 2. p. 789.

[5] Op. cit. p. 116.

silver dissolved in ammonia-water; and from such a solution tin throws down metallic silver upon the sides of the vessel.[6]

General remarks on the reduction of chloride of silver in water by metals.—According to Fischer, the action is generally such that the reduced silver attaches itself to the chloride of silver, and not to the reducing metal, as it does when reduced from solutions of soluble salts of silver; or, more correctly stated, the chloride of silver is converted into metallic silver without changing its form, whilst the compound of chlorine and the reducing metal dissolves in the water in so far as it may be soluble therein. The silver precipitated by several metals is not pure, but is intimately alloyed with the reducing metal: this is especially the case with zinc, lead, and antimony; and with antimony an alloy is produced in very beautiful broad plates, of which the crystalline form is quite different from that of silver.[7]

SILVER-PLATING.—Chloride of silver has been applied as an agent for plating, say brass, with silver. An old receipt is the following: mix 1 part by weight of precipitated and washed chloride of silver with 3 parts of common carbonate of potash (pearl-ash), 1 part of washed whiting, and somewhat more than 1 part of common salt. Clean the surface of the brass article to be plated, and remove all grease by rubbing with a piece of felt and rottenstone; then moisten it with salt and water, and rub on a little of the composition with the finger, when the surface will become very thinly silvered. Wash it well, rub it dry with a soft rag, and coat with transparent varnish. This mode of plating has only been used for clock faces, barometer scales, and similar objects.[8]

ACTION OF CERTAIN SULPHIDES ON CHLORIDE OF SILVER.

Without the presence of any other liquid than water.

It has been shown by Malaguti and Durocher that chloride of silver is directly decomposed, at ordinary temperatures, by contact with various metallic sulphides, when no other liquid than water is present.[9] Thus, when a mixture of sulphide of cadmium and chloride of silver is triturated with water, it soon loses the yellow colour due to the sulphide, becoming first bistre-coloured and finally black; and now, if the whole be thrown upon a filter, a solution of chloride of cadmium will pass through. A similar result was obtained with other sulphides, except that, occasionally, there was no appearance of reaction until after the lapse of a considerable time. It was only at the end of a month, for example, that the water in a pasty mass of chloride of silver and copper-pyrites became blue, owing to the formation of chloride of copper; and in a comparative experiment, made without the presence of chloride of silver, no such blue coloration was observed. Bisulphide of tin, under the same conditions, became black, and the water of the mixture contained much free hydrochloric acid; and the same result, it is stated, occurred in a like experiment

[6] Fischer, op. cit. p. 118.
[7] Op. cit. pp. 116, 122.
[8] Aikin's Dictionary, 2. p. 325.
[9] Op. cit. pp. 268-270.

with native cuprous sulphide, save that in this case the water became at once both acid and blue. In another part of their volume (p. 282), Malaguti and Durocher make the following remarks with respect to the case of bisulphide of tin :—

"If a mixture of water, chloride of silver, and well-washed mosaic gold [*i.e.*, bisulphide of tin] is left in the dark for a long time, it will be observed that the latter becomes black and the water becomes very acid, without however containing a sensible quantity of chloride of tin. This indicates that already the chloride of silver is decomposing, but without reacting upon the sulphide by way of double decomposition. On closer investigation, it will be perceived that the bisulphide is changed into protosulphide, and that at the same time sulphide of silver is produced. Mosaic gold, blackened by a solution of chloride of silver in ammonia-water, has its yellow colour immediately restored by contact for a few minutes with concentrated hydrochloric acid, and the acid liquor is found to contain tin, and the insoluble matter chloride of silver. This experiment, then, proves that the black substance with which mosaic gold becomes coated by contact with chloride of silver, consists of sulphide of silver and protosulphide of tin; whence it must be concluded that the decomposing faculty of certain sulphides may be exerted in the way of reduction: in this category are those sulphides which pass to a lower degree of sulphurization, by yielding part of their sulphur to the silver of the chloride." From the foregoing description it appears that sulphur is alone concerned in this reaction; and, if this be so, the question naturally arises whether sulphur in the free state would not act in like manner upon chloride of silver; but this, it is rather surprising, does not seem to have presented itself to Malaguti and Durocher. Now, if sulphur can thus directly decompose chloride of silver, chlorine must be liberated; and as chlorine decomposes sulphide of silver, it is difficult to understand how chloride of silver should be decomposed by sulphur; and further, no explanation is given of the reaction by which hydrochloric acid was found. It will probably be found that the reactions which occurred in the experiment were incompletely investigated.

With the presence of other liquids than water.

Disulphide of copper (*cuprous sulphide*).—When a solution of chloride of silver in ammonia-water is brought in contact with this sulphide, decomposition quickly occurs, according to Karsten, with the formation of metallic silver, chloride of copper, and sulphide of copper.[1] But when the chloride of silver is dissolved in a solution of chloride of sodium there is no action. The following equation probably expresses the above reaction as understood by Karsten :—

$$AgCl + Cu^2S = Ag + CuCl + CuS.$$
$$[2AgCl + Cu^2S = 2Ag + CuCl^2 + CuS.]$$

[1] Op. cit. p. 184. The sentence is obscurely worded, and the word "Schwefelkupfer" is used, apparently, to indicate Cu^2S and CuS.

The following experiment was made by Malaguti and Durocher.[2] Native cuprous sulphide, previously deprived by means of ammonia-water of traces of oxide on its surface, was mixed with twice its weight of chloride of silver, and the mixture was shaken in ammonia-water during several minutes. The liquor became intensely blue, whilst the solid portion acquired a whitish aspect and increased considerably in bulk. The whole was thrown upon a filter, and in the filtrate hydrochloric acid was found, and that it contained copper was evident from its colour. The substance left on the filter was a mixture of metallic silver, sulphide of silver, matrix, and mineral unacted upon. Malaguti and Durocher proposed the following equation in explanation of the reactions which occurred :—

$$2AgCl + Cu^2S = Ag + AgS + 2CuCl.$$
$$[4AgCl + Cu^2S = 2Ag + Ag^2S + 2CuCl^2.]$$

It will be perceived that this equation differs from that of Karsten stated above, according to which, cupric sulphide is formed, but no sulphide of silver. These reactions obviously need further investigation.

In another experiment 0·361 gramme (two equivalents) of chloride of silver was dissolved in ammonia-water, and to this solution was added 0·100 gramme (one equivalent) of pure cuprous sulphide prepared in the dry way. The mixture was shaken and poured upon a filter: the filtrate still retained 0·024 gramme of chloride of silver. What remained on the filter, a mixture of silver and sulphide of silver, weighed 0·250 gramme; the solution of this mixture in nitric acid contained a little copper. The quantity of chloride of silver remaining in the ammoniacal solution indicated that $\frac{1}{10}$th of the mineral (*sic*) had not been acted upon, which fact Malaguti and Durocher account for by supposing that the finely-divided silver, in a sponge-like state, might have enveloped a portion of the mineral and so have withdrawn it from all action. On the other hand, the solid product of the reaction should, according to calculation, have weighed 0·272 gramme, whereas it weighed only 0·250 gramme: on adding to the last number the quantity corresponding to that part of the mineral which escaped decomposition, and which amounts to 0·01632 gramme, the number 0·26632 is obtained; whence it results that while calculation indicates 272·00, experiment gave 266·32.

They concluded that the reaction between chloride of silver in solution and solid cuprous sulphide is as precise and almost as prompt as between two equivalent proportions of liquid substances.[3]

Sulphide of zinc.—Karsten states that in the presence of ammonia chloride of zinc is very soon formed, whilst the sulphur seems to combine with the silver; but when the chloride of silver is dissolved in an aqueous solution of chloride of sodium, the action on sulphide of zinc is retarded. Malaguti and Durocher found, to their surprise, that, on treating a mixture of blende and chloride of silver in small proportion with ammonia-water, not the slightest trace of the chloride

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[2] Op. cit. p. 283. [3] Op. cit. p. 284.

is thereby removed; and they ascertained that the disappearance of e chloride of silver was attended with the production of chloride of ic. They inferred that this was a case of double decomposition, chloride of silver having been changed into sulphide, and the phide of zinc into chloride. If this be so, the non-removal of ver by ammonia-water is explained, for sulphide of silver is oluble in that liquid.[4]

Malaguti and Durocher heated to whiteness [!], for two hours and alf, chloride of silver, placed in the bottom of a crucible, mixed h salt in order to assist its volatilization, and so arranged that its our passed through an overlying stratum of blende. On subse-ntly examining the particles of blende, they exhibited a partial entiferous coating, which was neither chloride of silver nor metallic er; whence they inferred that it was very probably sulphide of er, formed by double decomposition;[5] the reaction being as ows:—

$$AgCl + ZnS = AgS + ZnCl.$$
$$[2AgCl + ZnS = Ag^2S + ZnCl^2.]$$

Sulphide of lead.—According to Malaguti and Durocher, chloride silver, dissolved in ammonia-water, is decomposed by sulphide of d, with the formation of sulphide of silver and chloride of lead; l the same result occurs with chloride of silver dissolved in an ieous solution of hyposulphite of soda. Karsten, however, states t sulphide of lead has as little action as sulphide of bismuth on oride of silver, whether ammonia-water or solution of chloride sodium be the solvent;[6] by which, I presume, is meant there is ctically no action.

Malaguti and Durocher heated an intimate mixture of 1·5 gramme one equivalent) of sulphide of lead with 1·8 gramme (or one ivalent) of chloride of silver during an hour to a high tempera-re; whereby a small button was obtained, which weighed 1·85 amme, and was composed of two very distinct portions, a central re and an external layer. The latter was black and formed of illiant cubical plates; it was malleable and resisted pulverization. e central portion was less black, and presented a granular appear-ce; but, by the aid of a strong lens, cubical facets could be distin-ished. It appeared to be even more malleable than the external rtion. Analysis showed that sulphide of silver was present in rger quantity in the central than in the external part; and that roughout the mass a greater amount of it was present than of lphide of lead; whence it was inferred that double decomposition d taken place.[7] The loss may be attributed to the volatilization chloride of lead.

This reaction has been confirmed by H. Louis in my laboratory 876):—A mixture of chloride of silver and sulphide of lead (in omic proportions) was fused in a hard-glass tube at a dull red-heat.

[4] Op. cit. p. 268.
[5] Op. cit. p. 311.
[6] Karsten, op. cit. p. 184.
[7] Op. cit. p. 310.

There was a slight white sublimate, but the temperature was n sufficiently high to volatilize a sensible quantity of chloride of lea When cold, the tube was broken open, and the fused mass was fou to consist of two layers. The upper one was brittle, grey, a slightly vesicular; on boiling with water it almost wholly dissolve a black residue was left, and the solution contained chloride of lea The lower layer was black, dense, and very sectile; it dissolved nitric acid, and consisted chiefly of sulphide of silver: it contain 72·53% of silver, whereas pure sulphide of silver contains 87·1%. T reaction is as follows:—

$$AgCl + PbS = AgS + PbCl.$$
$$[2AgCl + PbS = Ag^2S + PbCl^2.]$$

Sulphide of mercury.—Heated with cinnabar, sulphide of silver a chloride of mercury (corrosive sublimate) are stated to be produce thus:—

$$AgCl + HgS = AgS + HgCl.$$
$$[2AgCl + HgS = Ag^2S + HgCl^2.]$$

Further experiments of Malaguti and Durocher upon chloride of sil and various sulphides and other compounds.—Malaguti and Durocb experimented upon what they designate the decomposing facul of various sulphides (for the most part natural minerals), arsen sulphides, etc.; and their mode of proceeding may be here fitting described, because, in their own account of their process, they ha presented the detailed results which they obtained by operating up galena as examples.

1. To 0·2 gramme of seleniferous galena from Beresow w added 7 cubic centimetres of a titrated ammoniacal soluti of chloride of silver, containing 0·002 gramme per cubic c timetre. After 18 hours of contact, the liquor, after addition of nitric acid, remained limpid.
2. Of the same galena 0·2 gramme, and of the same titra solution 8 c. c., were used. After 18 hours of contact, liquor, after the addition of nitric acid, still remained limp
3. Of the same galena 0·2 gramme, and of the same titra solution 9 c. c., were used. After 18 hours of contact, solution whitened considerably on the addition of nitric ac

The decomposing faculty, consequently, of this galena is re sented by 8; that is to say, 100 parts of the mineral decompos under the conditions stated, 8 parts at least of chloride of silver.

Check-experiments.

4. Of the same galena 0·2 gramme was mixed with 0·016 gram of chloride of silver and 8 c. c. of ammonia-water. After hours of contact, the liquor did not become turbid on addition of nitric acid.

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[a] Gmelin's Handbook, 6. p. 165.

5. Of the same galena 0·2 gramme was mixed with 0·017 gramme of chloride of silver and 8 c. c. of ammonia-water. After 18 hours of contact, the liquor whitened much on the addition of nitric acid; whence is deduced 8 as expressive of the decomposing faculty, *i.e.* the same number as previously obtained with titrated solutions of chloride of silver.

It is inferred that in the foregoing reaction there was simply an interchange of the so-called electro-negative elements of the chloride of silver and the sulphide of lead, resulting in the formation of sulphide of silver and chloride of lead; for weak acetic acid extracted oxide of lead from the insoluble matter, thus showing that chloride of lead had been produced and then decomposed by the ammonia, with the separation of oxide of lead, which is not soluble in ammonia-water.

By substituting an aqueous solution of hyposulphite of soda for ammonia-water as a solvent for chloride of silver, and operating in the manner above described, "sensibly identical" results were obtained; thus showing that the "decomposing faculty" of the sulphide or other substance experimented upon is not affected by the nature of the solvent used for the chloride of silver. By way of example, the following details of experiments upon artificial galena [by which, I presume, is meant fused artificial sulphide of lead] may be inserted:—

1. Of artificial galena (of which the "decomposing faculty" had been found equal to 5, with ammonia-water as the solvent) 0·5 gramme was mixed with 0·025 gramme of chloride of silver and 10 c. c. of an aqueous solution of hyposulphite of soda, containing 0·1 gramme of the salt per cubic centimetre. After 18 hours of contact, the liquor did not whiten copper.
2. Of the same galena 0·5 gramme was mixed with 0·026 gramme of dry chloride of silver and 10 c. c. of an aqueous solution of hyposulphite of soda, containing 0·1 gramme of salt per cubic centimetre. [It will be remarked that the chloride of silver in this instance is stated to have been dry; but it may fairly be presumed that in the other instances in which hyposulphite of soda was the solvent, it was also used dry; for, otherwise, without having recourse to a roundabout process, how could it have been weighed unless dry?] After 18 hours of contact, the liquor whitened copper immediately. The "decomposing faculty," consequently, was equal to 5, which is the same as that found when an ammoniacal solution of chloride of silver was used.

With regard to the use of a strip of metallic copper for ascertaining the presence of silver in the hyposulphite of soda solution (silver being deposited from such a solution upon the copper in the state of an adherent white dull metallic coating), the following experiments were made by Malaguti and Durocher in order to satisfy themselves that the presence of other metals did not interfere with the reaction. One milligramme of chloride of silver was dissolved in 10 c. c. of a solution of hyposulphite of soda, consisting of 9 parts of water

and 1 of the crystallized salt. A strip of copper immersed such a solution was whitened instantly; but when a strip of copp was immersed in an equal volume of the solution, not containi chloride of silver, it began to blacken after several hours of conta Three hyposulphite of soda solutions of chloride of silver were plac in contact with the sulphides of lead, tin, and antimony, respectivel The chloride of silver was added in such proportion that it might wholly decomposed; so that the solution should afterwards conta only lead, tin, or antimony. A strip of copper, cleaned with acid a subsequently washed with water, was immersed in each of tho solutions. After several hours of contact, each strip had becor coated with a film of tarnish (*s'est recouverte d'un voile terne*): a after the lapse of 18 hours, the strip in the lead solution had becor black; that in the tin solution had become black, but less so than the last instance; while that in the antimony solution had also becor black, but more so than the strip in the tin solution. On the oth hand, the same experiments were repeated with a solution of hyp sulphite of soda containing more chloride of silver than could wholly decomposed by contact with the three sulphides; so that t strips of copper, when immersed, were in contact with a solution hyposulphite of soda containing lead, tin, or antimony, and, besid silver in small quantity. Under these conditions, it was found th the strips of copper whitened forthwith, as if only silver had be present in the solution; but when tin or antimony was present, t precipitated silver was somewhat tarnished, while it retained its de whiteness in the solution containing lead. Hence it was inferred th hyposulphite of soda only acts upon metallic copper in the course time; that this metal causes the instant precipitation of the smalle quantity of silver from its solution in hyposulphite of soda; and th the presence of lead, tin, or antimony does not hinder the immedi precipitation of the silver.

It is, however, added that "the action of hyposulphite of so upon substances which do not admit of the use of ammonia is always *nil;* but its limits are so restricted, that it cannot sensi affect the results. Thus, for example, ammonia could not be employ to determine the decomposing faculty of sulphide of antimony; on examining a solution of hyposulphite which had been duri 24 hours in contact with that sulphide, it will be found to contai small portion of antimony. The same thing occurs with many ot sulphides; but the quantity attacked by the solvent is so feeble, t it exerts no appreciable influence upon the final result. The exp ment upon artificial galena, previously reported, proves that gal is slightly attacked by the hyposulphite; nevertheless, the value its decomposing faculty was found by the two processes to identical."

From the results of numerous experiments made by Malaguti a Durocher, in order to ascertain, in the manner previously describ the "decomposing faculty" exerted by various sulphides and certa other substances on chloride of silver, the following selection

presented:[3] the numbers in the column on the right indicate the number of parts by weight of chloride of silver decomposed in the course of 18 hours, under the conditions previously stated, by 100 parts by weight of the substance mentioned opposite to that number.

Simple Sulphides.

	Parts.
Artificial galena	5
Galena from Huelgoat	5
Galena very rich in silver from Freiberg	7
Seleniferous galena, with curved faces, from Beresow	8
Antimonial galena, with slightly curved faces, from Saint-Mandé	10
Arsenical galena, with the solid angles and the edges of the cube truncated, from Saxony	13
Seleniferous galena from Fahlun	13
Crystallized blende from Saxony	1
Sulphide of zinc, prepared in the dry way	3
Very pure blende from Kongsberg	3
Cadmiferous blende from Przibram	4
Fibrous blende from Pontpéan	5
Lamellar do. do.	5
Black artificial blende, obtained by sublimation	10
Artificial sulphide of cadmium	14
Cubical iron-pyrites	0·25
White or prismatic pyrites	0·50
White globular do.	1
Sulphide of cobalt, prepared in the dry way	6
Sulphide of nickel, do. do.	8
Sulphide of bismuth, do. do.	3·50
Protosulphide of tin, do. do.	0·33
Bisulphide of tin or mosaic gold	31
Sulphide of antimony	0·002
Sulphide of molybdenum	0·001
Native cinnabar	0
Sulphide of copper (cuprous sulphide) artificially prepared	337

Multiple Sulphides.

Copper-pyrites of unknown locality	10
Bornite or purple copper-ore, $3Cu^2S + Fe^2S^3$ [idem], from Sweden	10
Bornite, of a lilac tint, from Tunaberg	180
Cupro-nickeliferous pyrites from Espedal in Norway	2
Stromeyerite, $AgS + Cu^2S$ [$Ag^2S + Cu^2S$]	3·25
Compact bournonite	11

Arsenides, Arsenio-Sulphides, and Antimonio-Sulphides.

Smaltine	170
Kupfer-nickel	470
Mispickel, forming a fibrous mass	0·5
Crystallized mispickel from Utö	17·5
Nickel-glance from Schneeberg	440

The reactions which occurred in these latter cases do not appear to have been satisfactorily investigated.

It will be perceived that the "decomposing faculty" exerted by

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[3] Op. cit. p. 277.

various sulphides on chloride of silver varies not only with the sulphides of different metals, but also in some instances with varieties of the sulphide of the same metal. Malaguti and Durocher seem fully to have investigated this point; but as a satisfactory report of their experiments would occupy too much space in this volume, the reader who may desire further information on the subject must consult their original description in French. The general conclusion, however, at which they arrived is as follows:—The "decomposing faculty" of the sulphides may be modified by the state of purity, the density, the composition, the molecular state, the cohesion, the structure of the substance, and the crystalline form, even by modifications in crystals belonging to the *same* system of crystallization.[1]

They add that "in considering the causes which in the majority of cases restrict the limits of the action exerted by certain substances upon chloride of silver, it is not easy, for example, to explain why 100 parts of artificial cuprous sulphide decompose 360 parts of chloride of silver, *i.e.* one equivalent for two, whilst 100 parts of artificial sulphide of lead, on the contrary, only decompose 5 parts, *i.e.* $\frac{1}{24}$th part of what ought to be decomposed if the action were complete and occurred between atom and atom. In general, decomposition is rapid and almost instantaneous; and if it continue, it goes on so slowly as to escape detection. It should be observed that when there is double decomposition, the action is limited; and that, on the contrary, it is complete or at least it is very decided when there are phenomena of reduction. . . . . The highest numbers indicating 'decomposing faculty' belong to those substances which appear to decompose the chloride of silver by virtue of a reducing action. Thus cuprous sulphide, certain double sulphides of copper and iron, and bisulphide of tin, give much higher numbers than the sulphides of zinc, lead, iron, mercury, and antimony, which act by double decomposition. This circumstance has led us to suppose that when, in our experiments, sulphide of silver is formed by double decomposition, it adheres so much to the surface of the mineral as to coat it like a varnish; from that moment action is stopped, as there is no longer contact between the acting matters; but if we remove this varnish, action recommences. In the case where silver is precipitated in the metallic state, or even in the state of sulphide, but under conditions in which it will not be able to adhere strongly, nothing will prevent the continuance of the action, since there is no cessation of contact."

With regard to the modes of action of metallic sulphides on chloride of silver, Malaguti and Durocher assert that there are three kinds, as follow:[2]—

(1.) Double decomposition—

$$RS + AgCl = AgS + RCl.$$
$$[RS + 2AgCl = Ag^2S + RCl^2.]$$

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[1] Op. cit. pp. 302, 304.

[2] Op. cit. p. 285.

(2.) Reduction to a lower sulphide—

$$RS^2 + AgCl = AgS + RS + Cl.$$
$$[RS^2 + 2AgCl = Ag^2S + RS + 2Cl.]$$

(3.) Double decomposition and reduction—

$$R^2S + 2AgCl = Ag + AgS + 2RCl.$$
$$[R^2S + 4AgCl = 2Ag + Ag^2S + 2RCl^2.]$$

MISCELLANEOUS REACTIONS WITH CHLORIDE OF SILVER.

Chloride of silver and sulphuric acid.—It is not acted upon at ordinary temperatures by dilute or strong sulphuric acid; but when boiled with the strong acid, such as common oil of vitriol, it is wholly decomposed with the formation of sulphate of protoxide of silver. This has been recently published as novel information;[3] but I may state that the fact was demonstrated in my laboratory about 20 years ago, and that I have yearly announced it in my lectures since that time. Native chloride of silver is, however, only very slowly attacked even by the strong boiling acid. When boiled even with very dilute sulphuric acid, hydrochloric acid, it is stated, will be found in the distillate.[4]

Chloride of silver and sulphate of protoxide of iron (ferrous sulphate).—Wetzlar states that solid chloride of silver is not reduced by ferrous salts;[5] and recently precipitated moist chloride of silver, according to H. Rose, is not decomposed by ferrous sulphate.[6] Keir had long before announced, that "luna cornea is not decompounded by martial vitriol."[7]

Chloride of silver and sulphur.—Berthier states that when it is heated with sulphur, it is decomposed in small quantity, and forms what he designates a sulpho-chloride, which is greyish black, feebly metallic in lustre, lamellar like galena, but soft.[8]

Chloride of silver and sulphide of silver.—When these substances are melted together the product is apparently homogeneous, and continues so after solidification. When cold this product is black, and chloride of silver is dissolved out of it by ammonia-water. This observation is founded on an experiment on a very small scale; and possibly a much larger mass of the product, especially if slowly solidified, might have shown some degree of separation between the chloride and sulphide of silver.

Chloride of silver and phosphorus.—According to H. Rose, when chloride of silver is heated with phosphorus, chloride of phosphorus is evolved and metallic silver is separated, "with which a considerable quantity of chloride remains mixed" [that, surely, will depend on the temperature].[9]

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[3] Jahresber. 1873. p. 290.
[4] Handwörterb. 7. p. 938.
[5] Schweigger's Jahrbuch der Chemie und Physik, 1827. 21. p. 373.
[6] Chemical Gazette, 1847. 5. p. 2.
[7] Phil. Trans. 1790. 8. p. 384.
[8] Tr. des Ess. 2. p. 788.
[9] Gmelin's Handb. 6. p. 164.

Chloride of silver and phosphuretted hydrogen.—According to H. Rose, when chloride of silver is heated in this gas, metallic silver and phosphorus are separated, and hydrochloric acid is formed: the reaction takes place easily.[1]

Chloride of silver and litharge.—Berthier states that it melts in all proportions with litharge; and on the addition of galena to the molten mixture, the chloride of silver is wholly reduced to the metallic state, by the lead set free according to the reaction[2]:—

$$2PbO+PbS = 3Pb+SO^2 \text{ [idem]}.$$

Chloride of silver and cuprous oxide.—Cuprous oxide exerts no appreciable action on chloride of silver in water even at 100° C.;[3] but it is quite otherwise if, at the same temperature, alum, ferrous sulphate, or cupric sulphate be present. However, the reducing action of cuprous oxide, even with the concurrence of one of these sulphates, is less energetic than that of iron or copper, with or without the presence of such salts.

Chloride of silver and anhydrous boracic acid.—According to Berthier, the chloride is decomposed, but only in the presence of the vapour of water.[4]

Chloride of silver, borax, and siliceous fluxes.—It is stated to dissolve in small quantity in melted borax and in siliceous glasses,[5] to which, as is well known, it communicates opalescence and various tints from yellow to brown; but it is questionable whether this is true solution. The point will be further considered under the head of Silver and Silicon.

Chloride of silver and carbonic oxide.—When heated in a current of carbonic oxide, chloride of silver is stated to be quickly reduced to the metallic state with the formation of chloro-carbonic acid or phosgene gas, thus[6]:—

$$AgCl+CO = Ag+COCl.$$
$$[2AgCl+CO = 2Ag+COCl^2.]$$

Hypochlorite of Silver, AgO,ClO [AgClO].

According to Stas, when, under the influence of constant agitation, a current of chlorine is slowly passed into water, containing an excess of oxide or carbonate of silver in suspension, chloride of silver and hypochlorous acid are formed. But this acid remains only momentarily free, and slowly changes part of the suspended oxide or carbonate into hypochlorite of silver, which is very soluble in water. This salt is stated to be pretty stable in the presence of an excess of oxide or carbonate of silver, and may thus be preserved during several days; whereas, in the absence of either of those substances,

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[1] Gmelin's Handb. 6. p. 164.
[2] Tr. des Ess. 2. p. 790.
[3] Malaguti and Durocher, op. cit. p. 388.
[4] Tr. des Ess. 2. p. 789.
[5] Berthier, op. cit. 2. p. 790.
[6] Göbel, Gmelin's Handb. 6. p. 164.

it is extremely unstable. When the liquid is left at rest, it becomes very turbid as soon as the oxide or carbonate has subsided, chloride of silver being deposited and chlorate of silver remaining in solution. Stas supposes that successive reactions occur, which may be represented by the following equations:—

$$2Cl + AgO + HO = AgCl + HO,ClO.$$
$$HO,ClO + AgO = AgO,ClO + HO.$$
$$3(AgO,ClO) = 2AgCl + AgO,ClO^5.$$
$$[4Cl + Ag^2O + H^2O = 2AgCl + 2HClO.]$$
$$[2HClO + Ag^2O = 2AgClO + H^2O.]$$
$$[3AgClO = 2AgCl + AgClO^3.]$$

By the action of an *excess* of saturated chlorine water upon oxide or carbonate of silver, the silver is completely changed into chloride, and the liquid contains only the residual chlorine, without a trace of either chloric or perchloric acid.[7]

Chlorite of Silver, AgO,ClO^3 [$AgClO^2$].

It is prepared by the addition of an aqueous solution of an alkaline chlorite, containing excess of base, to an aqueous solution of nitrate of silver, when the salt is thrown down in admixture with oxide of silver. The precipitate is boiled with water, which dissolves the chlorite and not the oxide of silver. On cooling, the salt separates in the form of yellow scales. It explodes at 105° C.; and, by stirring a mixture of it and sulphur with a glass rod, ignition takes place.[8]

Chlorate of Silver, AgO,ClO^5 [$AgClO^3$].

One mode of formation of this salt has been described under the head of Hypochlorite of Silver, namely, by passing chlorine into water containing oxide or carbonate of silver in suspension. Stas has prepared it in considerable quantity by that mode. Oxide of silver is to be preferred to carbonate for this purpose. The solution of hypochlorite of silver is spontaneously decomposed, with the formation of chloride and chlorate of silver; and the decomposition is promoted by heating the solution to 60° C. Obtained by evaporating its aqueous solution to dryness, it is as unchangeable in pure moist air as chlorate or sulphate of potash; but if it contains any perchlorate of silver, which is deliquescent, it attracts moisture from the air.[9] If its solution is evaporated until a pellicle forms on its surface and then left to cool, it is deposited in white opaque crystals. It melts at a gentle heat, and at a higher temperature is resolved into chloride of silver and oxygen. When it is triturated with sulphur, there

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[7] Nouvelles Recherches, etc. antea cit. p. 92.

[8] Mémoire sur les Combinaisons oxygénées du Chlore. Par M. Millon. Ann. de Chim. et de Phys. 1843. 3 ser. 7. p. 329.

[9] Nouvelles Recherches, etc. antea cit. pp. 94 et seq. The preparation of the chlorate of silver is stated with the fullest details. See also Berzelius, Tr. de Chim. 4. p. 280; Gmelin's Handb. 6. p. 167.

is explosion. It is not changed by exposure to light. It is very soluble in water, cold as well as hot; but trustworthy information as to its degree of solubility is wanting. According to Stas, a current of sulphurous acid precipitates sulphite of silver from an aqueous solution of chlorate of silver, and chloric acid is set free; and it is only by the prolonged action of the sulphurous acid upon the chloric acid, that the sulphite of silver is converted into chloride.

Perchlorate of Silver, AgO,ClO^7 [$AgClO^4$].

It may be prepared by digesting oxide of silver with aqueous perchloric acid, and is left in the state of white powder by evaporating the solution to dryness. It is very deliquescent, and is soluble in absolute alcohol. Its aqueous solution is said to become brown on exposure to sunlight. It is fusible, but if heated to a certain degree beyond its melting-point, which is somewhat below redness, it is suddenly resolved into chloride of silver and oxygen. It is crystalline after fusion. Paper saturated with it and dried, is stated to detonate violently at 200° C.[1]

SILVER AND BROMINE.

Combination between these elements speedily occurs at ordinary temperatures, as may be well shown by loosely filling a bottle with silver leaf, and introducing a few drops of bromine or by immersing silver leaf in an aqueous solution of bromine. The product is bromide of silver, AgBr [idem]. This salt may be conveniently prepared by adding an aqueous solution of bromide of potassium to a similar solution of nitrate of protoxide of silver, when it is precipitated. Thus made, it is a pale yellow powder, and melts easily into a red liquid which solidifies into a translucent, deep yellow mass, having a crystalline fracture: in thin layers it is said to be quite transparent. On cooling it emits loud cracking sounds. It becomes brittle even before it is quite cold. Its sp. gr. is, according to Karsten, 6·353; but Rodwell found the sp. gr. at 7° C. of a specimen which had been once fused to be 6·293, and that of a specimen which had been often fused to be 6·245.[2] It is insoluble in water. It is soluble in a cold strong aqueous solution of bromide of potassium, in cold aqueous solutions of hyposulphite of soda and cyanide of potassium, in strong ammonia-water but less easily than chloride of silver, sparingly in an aqueous solution of carbonate of ammonia, in a hot aqueous solution of chloride of ammonium, slightly in sulphuric acid from which it is thrown down by the addition of water, and in strong hydrobromic or hydrochloric acid. It is insoluble either in hot or cold nitric acid. It is not acted upon by boiling nitric acid, but boiling sulphuric acid decomposes it with the formation

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[1] Berzelius, Tr. de Chim. 4. p. 280. Gmelin's Handb. 6. p. 167.

[2] Proceedings of the Royal Society, 1876. 25. p. 289.

sulphate of silver and evolution of vapour of bromine. It is completely reduced like chloride of silver by fusion with carbonate of soda, or by zinc in the presence of water acidified with hydrochloric acid. Heated in a current of chlorine, bromide of silver is changed into chloride; and the same change is stated to result from the action of chlorine-water upon the bromide.[3] But the last statement needs confirmation; for, according to Field, when a mixed solution of bromide of potassium and chloride of sodium is added gradually to a solution of nitrate of silver, not in excess, no trace of chloride of silver is precipitated, so long as any bromide remains in solution; and when chloride of silver is put into a solution of bromide of potassium, complete decomposition ensues, bromide of silver and chloride of potassium being produced. Whence it is inferred that bromine has a stronger affinity than chlorine for silver.[4] In a series of photographic experiments made by my friend Mr. George Shaw and myself in 1844, we placed a flat piece of glass, with dry chloride of silver adhering to its surface, in a glass tube containing a few drops of bromine, and then hermetically sealed the tube. A considerable time afterwards the tube was opened and the chloride of silver seemed to have been changed into bromide, as it had acquired a pale yellow colour and did not darken on exposure to light; but no analysis was made. Pure bromide of silver undergoes no *visible* change by exposure to sunlight.

SILVER AND IODINE.

Combination between these elements takes place at ordinary temperatures, and the product is iodide of silver, AgI [idem]. This salt may be conveniently prepared by adding an aqueous solution of nitrate of protoxide of silver to a similar solution of iodide of potassium, when it is precipitated. Thus made it is a pale yellow powder. Silver dissolves in cold hydriodic acid with the evolution of hydrogen; and when the acid is concentrated, the action is violent. The action continues until the liquid is saturated with iodide of silver; and on the application of heat it again proceeds. On cooling, large colourless crystalline plates are deposited, which decompose as soon as they are taken out, and which are supposed to be a compound of iodide of silver and hydriodic acid. After the removal of these crystals, the liquid on standing yields tolerably thick hexagonal prisms of iodide of silver, which exactly resemble the native iodide. Concentrated hydriodic acid decomposes chloride of silver with the production of heat and the evolution of hydrochloric acid. According to Field, when a mixed solution of iodide, bromide, and chloride of potassium is added to a solution of nitrate of silver, not in excess, iodide of silver only and nitrate of potash are formed; when chloride

[3] See Berzelius, Tr. de Chim. 4. p. 264; Gmelin's Handb. 6. p. 159; Storer's Dict. of Solubilities, p. 81; and Handwörterbuch, 7. p. 932.

[4] Chem. Gazette, 1857. 15. p. 318.

of silver is put into a solution of iodide of potassium, iodide of silver and chloride of potassium are formed; when bromide of silver is put into a solution of iodide of potassium, iodide of silver and bromide of potassium are formed; when chloride of silver in excess is agitated with a solution of iodide of potassium and warmed for some hours, no trace of iodine can be detected in the solution; and when iodide of silver is put into a solution of chloride of sodium or of bromide of potassium, the iodide is not acted upon.[5] Whence it is inferred that iodine has a stronger affinity than chlorine or bromine for silver. An aqueous solution of iodide of potassium in contact with metallic silver becomes alkaline, and iodide of silver is formed. When metallic silver is heated to cherry-redness in a porcelain crucible with molten iodide of potassium, iodide of silver is also formed, and the potassium set free acts upon the crucible, forming silicate of potash and silicon.[6] It melts easily—at 450° C. according to Rodwell[7]—into a red liquid, which solidifies into an opaque yellow mass; but when it is strongly heated, it is partially decomposed, with the evolution of iodine, though it volatilizes unchanged when heated to whiteness in a closed vessel.[8] Rodwell states that "it solidifies to a perfectly transparent, very flexible, claret-coloured mass," which, on further cooling, becomes amber-coloured, and then just above 142° C. pale yellow: at this temperature it passes from the amorphous to the crystalline state, at the same time expanding considerably and becoming opaque, brittle, and pale-green.[1] According to Karsten, its sp. gr. is 5·0262, and, according to Boullay, 5·614: Rodwell found the sp. gr. of a specimen which had been only once fused to be 5·66, and that of a specimen which had been many times fused to be 5·675.[2] It is insoluble in water. It is soluble in a cold aqueous solution of iodide of potassium, containing about 9 or 10 times its weight of the latter, and is precipitated therefrom by the addition of water; in a hot aqueous solution of potash, and when boiled in such a solution it is not decomposed, though, according to A. Vogel, it becomes grey-coloured in consequence of a mere molecular change;[3] in cold strong aqueous solution of hyposulphite of soda, and in a weak one with the aid of heat; in an aqueous solution of cyanide of potassium; in 2510 parts of ammonia-water of sp. gr. 0·96; and in hydriodic acid if not too dilute. It is stated to dissolve in notable quantity in strong aqueous solution of chloride of potassium or sodium; but as iodide of potassium precipitates iodide of silver from an aqueous solution of chloride of sodium in which chloride of silver is dissolved, iodide of silver must be less soluble than chloride of silver in such a solution of chloride of sodium. The use of iodide of potassium for precipitating silver in the state of iodide from a solution of chloride of sodium, containing a small quantity of chloride of silver dissolved, has been

[5] Chem. Gazette, 1857. 15. p. 318.
[6] H. Sainte-Claire Deville, Jahresber. 1856. p. 412.
[7] Proceedings of the Royal Society, 1876. 25. p. 286.
[8] A. Vogel, Jahresber. 1871. p. 342.
[1] Op. cit. p. 287.
[2] Op. cit. p. 288.
[3] Jahresb. 1871. p. 341.

patented by F. Claudet. Iodide of silver is insoluble in dilute sulphuric or nitric acid, and is decomposed by these acids when concentrated, with the evolution of vapour of iodine. It is stated to be completely reduced by fusion with carbonate of soda; but A. Vogel asserts that it is only very imperfectly reduced when fused with potash.[4] The same chemist also states that when it is acted upon by zinc in the presence of water acidified with hydrochloric acid the separation of metallic silver is not so complete as in the case of chloride of silver. Heated in a current of chlorine it is changed into chloride of silver.[5] By the action of mixed aqueous hydrochloric and hydriodic acids on metallic silver, only iodide of silver is produced.[6] When pure, iodide of silver undergoes no *visible* change on exposure to sunlight.

SILVER AND FLUORINE.

According to Gay-Lussac and Thénard, aqueous hydrofluoric acid does not act upon metallic silver, but readily dissolves oxide of silver, forming fluoride of that metal, AgF [idem]. This salt has a very strong metallic savour, is extremely soluble in water, is slightly deliquescent, is not volatile, and does not crystallize. When heated, it melts, loses its excess of acid, and afterwards continues to be soluble in water. It blackens the skin. It is decomposed by hydrochloric acid; and "all the salifiable bases precipitate oxide of silver from it, except ammonia."[7] Heated with access of air beyond its melting-point, the molten mass acquires a coating of metallic silver, which becomes thicker and thicker; and this reduction is attributed to the action of the moisture in the air, whereby hydrofluoric acid and oxygen are evolved, as indicated in the equation—

$$AgF + HO = Ag + HF + O.$$
$$[2AgF + H^2O = 2Ag + 2HF + O.]$$

Fluoride of silver is decomposed by chlorine at a red-heat with the formation of chloride of silver.[8] Gore has published the results of a series of experiments upon the formation and properties of fluoride of silver.[9] He states that it is not only slightly but very deliquescent; and that it may be crystallized from solution as a hydrous salt. Gore's papers contain some remarkable statements concerning the properties of fluoride of silver; but whether they have been confirmed by other chemists I am not aware.

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[4] Op. cit. p. 341.

[5] See Berzelius, Tr. de Chim. 4. p. 264; Gmelin's Handb. 6. p. 157; Storer's Dict. of Solubilities. p. 332; and Handwörterbuch, 7. p. 948.

[6] Deville. Loc. cit. p. 412.

[7] Recherches Physico-Chimiques, 1811. 2. p. 33. See also Scheele's Chem. Essays, London, 1786. p. 28; Berzelius, Tr. de Chim. 4. p. 266; and Gmelin's Handb. 6. p. 168.

[8] The Collected Works of Sir H. Davy, 1840. 5. p. 420.

[9] Proc. Roy. Soc., 1870. 18. p. 157; 19. p. 235.

SILVER AND CYANOGEN.

Cyanide of Silver, AgCy [idem].

It is precipitated in the state of white powder by the additi of hydrocyanic acid or cyanide of potassium to an aqueous sol tion of nitrate of silver; and it may be prepared by the action the latter solution upon various metallic cyanides. Its sp. gr. 3·943.[1] Scheele, its discoverer, stated "that silver is precipitate [by an aqueous solution of cyanide of potassium] of a white colou and of a consistence like that of cheese:" the precipitate was cyanid of silver.[2] When heated, it melts, loses half its cyanogen, and i converted into dicyanide of silver (argentous cyanide), which, at a higher temperature, is decomposed with the evolution of heat and light, nitrogen escaping and a supposed carbide of silver remaining. In the presence of water it is resolved by chlorine into chloride of silver and cyanogen; and it is decomposed by aqueous hydrochloric acid with the production of chloride of silver and hydrocyanic acid. When acted upon by an aqueous solution of chloride of mercury (corrosive sublimate), chloride of silver and cyanide of mercury are formed. Boiled with sulphuric acid somewhat diluted, cyanide of silver is changed into sulphate, and hydrocyanic acid is disengaged, by which means it may be separated from chloride of silver; but with the same acid concentrated or with strong nitric acid, cyanogen is evolved, and sulphate or nitrate of silver produced accordingly. When recently precipitated, it is stated to dissolve readily in a concentrated solution of sulphocyanide of potassium, from which solution water throws down crystalline sulphocyanide of silver.[3] Sulphuretted hydrogen transforms it into sulphide of silver, with the formation of hydrocyanic acid; and so does an aqueous solution of sulphide of potassium but in this case cyanide of potassium is produced instead of hydrocyanic acid. Sulphide of silver precipitated from a very dilute solution, is stated not to be insoluble in cyanide of potassium (see p. 21). Cyanide of silver is changed into chloride, when boiled with a aqueous solution of chloride of potassium or sodium. It is insoluble in water; but dissolves in aqueous solutions of hyposulphite of soda, cyanide of potassium or sodium (as Scheele, its discoverer, stated[4] ferrocyanide of potassium, ammonia, and various ammoniacal salts namely, carbonate, sulphate, nitrate, and chloride: from its solution in ammonia or salts of ammonia it is thrown down by acids. It is neither dissolved nor decomposed by an aqueous solution of caustic or carbonate of, soda. When free from chloride it does not blacken whether dry or moist, on exposure to sunlight. It combines with various metallic cyanides, forming double salts, of which one is of great value in Electro-Metallurgy, namely, the argento-cyanide of potassium.[6]

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[1] Jahresber. 1860. p. 17.
[2] Chemical Essays, London, 1786. p. 395.
[3] Chem. Gazette, 1851. 9. p. 386.
[4] Jahresber. 1853. p. 680.
[5] Op. cit.
[6] Gmelin's Handb. 8. p. 26. See also Baup, Sur les Cyanures Argentico-Alcalins. Ann. de Chim. et de Phys. 1853. ser. 53. p. 462.

Argento-Cyanide of Potassium, KCy,AgCy [idem].

It is always anhydrous. It is permanent in the air, does not affect the colour of litmus, is inodorous, and has a bitter savour. The crystals do not blacken on exposure to light. It dissolves in 4·7 parts by weight of water at 15° C., and its solubility greatly increases with the temperature; it dissolves in 25 parts of alcohol (of 85%) at 20° C., and from a boiling alcoholic solution it is deposited in fern-like crystals or in transparent hexagonal tables.[7] According to Rammelsberg, it crystallizes in regular octahedra. From its aqueous solution, sulphuretted hydrogen and the alkaline sulphides precipitate the silver in the state of sulphide; and the acids in common use, including acetic acid, throw down cyanide of silver. But no precipitate is produced in this solution by potash or soda or their carbonates, or by chloride of potassium or sodium. The argento-cyanide of potassium may be prepared in various ways: thus, by dissolving cyanide, chloride, carbonate, or oxide of silver in an aqueous solution of cyanide of potassium:[8]—

a. $2KCy + AgCl = KCy,AgCy + KCl.$
b. $2KCy + AgO,CO^2 = KCy,AgCy + KO,CO^2.$
c. $2KCy + AgO = KCy,AgCy + KO.$
a. [idem.]
b. $[4KCy + Ag^2CO^3 = 2(KCy,AgCy) + K^2Co^3.]$
c. $[4KCy + Ag^2O = 2(KCy,AgCy) + K^2O.]$

Metallic silver dissolves in a hot aqueous solution of cyanide of potassium but *slowly* and *sparingly*, as shown by the following experiment by R. Smith. A single silver leaf was heated during several hours in a concentrated aqueous solution of cyanide of potassium, and it was found that only a small quantity of silver had been dissolved. Christomanos, on the other hand, asserts that pure silver dissolves *readily* in a hot solution of this salt.[9] In this case hydrogen must be evolved according to the following equation, unless the silver is oxidized by oxygen derived from any cyanate of potash that might be present; though in the experiment by R. Smith above recorded no evolution of hydrogen was observed:—

$$2KCy + Ag + HO = KCy,AgCy + KO + H.$$
$$[4KCy + 2Ag + H^2O = 2(KCy,AgCy) + K^2O + 2H.]$$

Electro-plating by means of argento-cyanide of potassium.—The credit of the first application of this salt to this beautiful art, and the appreciation of its value for that purpose, is due to the late Mr. Alexander Wright, surgeon, of Birmingham. Mr. Wright informed me that he was led to this invention from reading the following passage in Scheele's memoir on Prussian Blue:[1]—

"It is remarkable, that our colouring matter [hydrocyanic acid],

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[7] Baup, Ann. de Chim. et de Phys. 3. ser. 1858. 53. p. 464.
[8] Gmelin's Handb. 8. p. 29.
[9] Fresenius' Zeitschrift für analytische Chemie, 1868. 7. p. 301.
[1] Chemical Essays. Translation by Dr. Beddoes. London, 1786. p. 405.

after it has united with the alkali, or with the lime, forms a menstruum, capable not only of dissolving metallic calces, but also constituting a triple salt, which is not decomposed by the aërial acid as happens with the lixivium, sanguinis [*i.e.* aqueous solution of cyanide of potassium] and the precipitating liquor, when exposed to the free access of air. Iron is not the only metal which has the property of fixing the colouring matter, the same quality belongs likewise to gold, silver, copper, and probably to several other metallic calces; for if, after these calces have been precipitated, a sufficient quantity of precipitating liquor be added, in order to redissolve them, the solution remains clear in the open air, and in this the aërial acid does not precipitate the metallic calx."

A patent was granted for the use of cyanide of potassium in electro-plating to Messrs. George Richards Elkington and Henry Elkington, in 1840,[2] Mr. Wright having sold his invention to those gentlemen on condition of receiving one shilling per ounce of silver deposited. The patent ought legally to have been taken out in the name of the inventor.

Argento-Cyanide of Sodium, NaCy,AgCy [idem].

It is anhydrous, and usually occurs in foliated crystals. It dissolves in 5 parts by weight of water at 20° C. and in 24 of alcohol (of 85%). In its chief properties it resembles the potassium salt. It may be prepared by melting ferrocyanide of sodium with half an equivalent of carbonate of soda, both being thoroughly dry. An aqueous solution of the cyanide of sodium formed is to be saturated with cyanide of silver.[3]

Argento-Cyanide of Potassium and Sodium, 3(KCy,AgCy) + NaCy,AgCy [idem].

It is anhydrous, and occurs in translucent, rhombic prisms. It dissolves in 4·4 parts by weight of water at 15° C., and in 22 of alcohol (of 85%) at 17° C. Baup maintains that it was this salt which Glasford and Napier erroneously described as a variety of argento-cyanide of potassium in rhombic prisms; and that its formation was due to the presence of carbonate of soda in the carbonate of potash added to the ferrocyanide of potassium used in the preparation of the cyanide of potassium. He supposes that the carbonate of soda may have naturally existed in the carbonate of potash, or have been fraudulently mixed with it. The argento-cyanide of potassium and sodium contains a little more silver than the argento-cyanide of potassium.[4]

Sulphocyanide of Silver, $AgCyS^3$ [AgCyS].

Sulphocyanide of silver (argentic sulphocyanate) may be prepared

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[2] Abridgments of Specifications relating to Electricity and Magnetism, 1855, p. 39. [3] Baup, loc. cit. [4] Op. cit. p. 465.

by adding an aqueous solution of nitrate of silver to a similar solution of sulphocyanide of potassium, when it is precipitated as a white curdy substance, which dissolves readily in an excess of the latter solution. It dissolves in ammonia-water with difficulty, and then not without the application of heat. It does not dissolve in water, in dilute acids, or in nitric acid, nor in a solution of sulphocyanide of ammonium or nitrate of silver. After having been well washed, it darkens in sunlight, but less than chloride of silver. Chlorine gas acts upon it while it is cold, but more energetically when heat is applied, and the products are chloride of sulphur, chloride of cyanogen, and chloride of silver. Chlorine-water also decomposes it, with the formation of chloride of silver, sulphur, ammonia, and carbonic acid. Freshly-precipitated argentic oxide dissolves in a solution of sulphocyanide of ammonium, with the evolution of ammonia; and from this solution hydrochloric acid precipitates sulphocyanide of silver. The sulphocyanides of the alkaline metals combine with sulphocyanide of silver, forming therewith double salts which are soluble in water: it combines also with sulphocyanide of ammonium. When a concentrated solution of sulphocyanide of silver in sulphocyanide of potassium is slowly evaporated under a jar, with the aid of sulphuric acid, large colourless rhombo-octahedral crystals of the double salt are formed: their composition is

$$KCyS^2 + AgCyS^2 \text{ [KCyS + AgCyS, or } KAgCy^2S^2\text{]}.$$

The crystals should be carefully freed from mother-liquor by draining. They are very bright, somewhat flexible, and unchangeable in the air. They are decomposed by water, sulphocyanide of potassium dissolving and pure sulphocyanide of silver being left. This double salt is not decomposed when heated up to 140° C., when it melts without decomposing; at a higher temperature it is decomposed and becomes black; by carefully prolonging fusion for some time, and washing the product with water, the sulphocyanide of silver is occasionally obtained in long prisms. According to Grossmann, when to a moderately concentrated solution of the double sulphocyanide of silver and of potassium or ammonium, ammonia is added, the entire solution soon becomes filled with thin plates of sulphocyanide of silver, which have a bright pearly lustre. If ammonia be poured upon the double salt, dried by evaporation, there is formed a substance which resembles in appearance chloride of silver, and soon changes into a beautiful crystalline magma, consisting of sulphocyanide of silver. Dilute hydrochloric acid produces a similar effect to that of ammonia, only the crystals in this case soon fall into a granular powder.[5]

Volhard recommends the volumetric determination of silver by means of sulphocyanide of silver, which he asserts is as insoluble as chloride of silver. To a solution of a salt of silver a little ferric

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[5] Handwörterb. d. Chemie, 1859. 7. p. 966. The preceding article on this subject is nearly a literal translation. See also Chemical Gazette, 1851. 9. p. 386; and 1857. 15. p. 25.

sulphate is added, and then a titrated solution of sulphocyanide of potassium or ammonium, until *permanent* blood-red coloration occurs. Although such coloration takes place on each addition of the sulphocyanide, yet it immediately disappears and continues to do so until the whole of the silver is precipitated as sulphocyanide of silver.[6]

SILVER AND NITROGEN.

Nitride of Silver.

It has been conjectured that fulminating silver, which results from the action of ammonia-water on oxide of silver, may be a nitride of the metal, possibly of the formula Ag^3N [idem]; but, owing to the highly explosive nature of that substance, it has been impossible to ascertain its composition with certainty.

Nitrate of Silver, AgO,NO^5 [$AgNO^3$].

It is colourless, and crystallizes in transparent, thin plates, belonging to the prismatic system of Miller. Its sp. gr. is given as 4·3554 by Karsten. It is anhydrous, does not redden litmus-paper, and has an intensely bitter taste. It is permanent in the air. It melts at a low temperature—according to Pohl at 198° C.[7]—without change in composition, and is crystalline and colourless after solidification, when it is known as *lunar caustic*, which is so much used by surgeons as an escharotic. It resists a temperature at which nitrate of copper (cupric nitrate) is decomposed, so that if it be contaminated with nitrate of copper, it may be freed from the latter by being kept fused at a suitable heat, until the effervescence due to the decomposition of the nitrate of copper has ceased, and the mass become tranquil, and then acting upon the product with water, which will dissolve the nitrate of silver and leave the copper in the state of insoluble protoxide. At incipient redness it is wholly reduced to the metallic state.[8]

Persoz has investigated the action of heat on nitrate of silver, with the following results. He found that before the salt reached the temperature of incipient redness, and while it was in tranquil fusion, bubbles of colourless gas (oxygen) were evolved from its midst, which soon acquired a slight reddish tint from the presence of nitrous vapour. In an experiment in a glass retort upon 15 grammes of nitrate of silver, the heating was stopped when 0·3 litre of pure oxygen gas had been collected. The product, which had a slight yellow colour, was treated with boiling water, when there was left a minute quantity of insoluble matter, which proved to be metallic silver. In the solution nitrite of silver was deposited in long, extremely fine needles; and the mother-liquor retained only nitrate of silver. It was demonstrated by other experiments, that the nitrite

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[6] Jahresber. 1874. p. 998.
[7] Idem, 1851. p. 59.
[8] Gmelin's Handb. 6. p. 168. Handwörterbuch, 8. p. 303, and 7. p. 170.

was formed during the process of heating, and not subsequently by the action of the reduced silver upon the boiling solution of the nitrate operated upon. The conclusions at which Persoz arrived are, that nitrate of silver is partially converted by heat into nitrite, and that the nitrite is only formed in the presence of a nitrate, which renders it stable, such as the nitrate of silver or of a fixed alkali.[1]

Nitrate of silver dissolves at 11° C. in 0·783 of its own weight of water,[1] and in half its weight of water at 100° C. It is insoluble in strong nitric acid, by which it is, accordingly, precipitated from its aqueous solution. Its solubility in water decreases as the proportion of free nitric acid increases. It is stated to dissolve in about 4 times its own weight of boiling alcohol.

Nitrate of silver is prepared by the action of nitric acid (somewhat diluted) on silver, and the action is much promoted by heat. According to Millon, silver is not attacked by nitric acid of lower sp. gr. than 1·405 (*i.e.* an acid containing 42·77% of water, and of which the composition is represented by $2NO^5 + 9HO$ [$2N^2O^5 + 9H^2O$]) at 20° C., so long as the temperature is not raised and no solution of nitrate is added; in pure and concentrated acid it becomes coated with a layer, sometimes grey and sometimes white, which stops the oxidation.[2] Should any copper be present, it may be separated as protoxide (cupric oxide) by digesting the solution with excess of oxide of silver, which may be formed by adding potash to one portion of the solution, washing the precipitate of oxides of silver and copper, and then digesting it with the other portion of the solution; or, strong nitric acid may be added to the solution, when nitrate of silver will be thrown down, while the nitrate of copper will remain dissolved: by then washing the precipitated nitrate of silver with strong nitric acid, it will be obtained perfectly free from copper. By adding carbonate of lime to an aqueous solution of nitrate of silver containing nitrate of copper, heated to about 70° C., so long as effervescence continues to be produced, the whole of the copper may be precipitated in the state of green carbonate, and the silver left in solution. For this purpose chalk mixed with water to a creamy consistency is directed to be used.[3]

Nitrate of silver suffers no discoloration by exposure to sunlight, except there be contact with organic matter.

When silver is suspended in pure nitric acid, and the liquid is looked at by transmitted light, it is perceived that the metal dissolves without evolution of gas, and a concentrated solution falls from the surface of the silver in dense striæ. The solution gradually becomes greenish, this colour being due to the reduction of nitric acid at a low temperature to nitrous acid, which remains in solution. The

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[1] Note sur la Décomposition du Nitrate argentique sous l'Influence de la Chaleur. Ann. de Chim. et de Phys. 3. s. 1848. 23. p. 48.

[1] Handwörterbuch der Chemie, 1859. 7. p. 171.

[2] Recherches sur l'Acide nitrique; par M. E. Millon. Ann. de Chim. et de Phys. 3. s. 1842. 6. p. 98.

[3] Gräger, Jahresber. 1872. p. 271.

liquid, however, soon becomes hot, and occasionally the silver dissolves suddenly with violent disengagement of gas.[4]

Detonation occurs when nitrate of silver is dropped on red-hot charcoal, or when in contact with phosphorus it is struck by a hammer on an anvil.

It is stated that nitrate of silver may be melted in iron vessels without change, provided water be absent;[5] and that when molten silver is separated in the metallic state by zinc, cadmium, tin and copper, though not at all, or very slowly, by [certain?] other metals.[6]

Silver is separated in the metallic state from the aqueous solution of its nitrate by lead, tin, cadmium, zinc, copper, bismuth, antimony, arsenic, and mercury. The time required for reduction varies with the kind of metal employed; it is shortest with the first two, and longest with the last two of this series. Reduction is equally effected by the metals above enumerated, except antimony, in the case of an alcoholic solution of nitrate of silver. According to Fischer, "iron causes no reduction either in an aqueous or alcoholic solution of nitrate of silver, provided the solution is perfectly neutral and there is no access of air; and none occurs so long as the metal is kept under the solution. If, on the contrary, the solution is not neutral, but is diluted to a certain degree and contains free acid, or, if the iron projects out of the solution and is exposed to atmospheric air, reduction always follows in a longer or shorter time, which depends partly upon the degree of dilution of the solution, as also upon the quantity of free acid, and partly upon the quality of the iron itself. However, under favourable conditions, complete reduction of the silver hardly occurs even after a very long time."[7]

Silver is reduced to the metallic state from the ammoniacal solution of its nitrate, quickly and completely by zinc, cadmium, copper, and arsenic; slowly by cobalt, mercury, and antimony; and not at all by iron, manganese, nickel, or bismuth.[8]

Wöhler states that when silver is immersed in a concentrated solution of nitrate of silver, overlaid with water, metallic silver is deposited in a dendritic form, always originating from a few scattered points on the surface of the silver.[9]

Dioxide of copper (cuprous oxide) throws down from a solution of nitrate of silver a grey substance, which consists of metallic silver and insoluble basic nitrate of copper; and nitrate of copper is found in solution: it behaves, in this case, in the same way as an *equal weight* of a mechanical mixture of metallic copper and cupric oxide would do, provided the former is equal in weight to the copper contained in the latter.[1]

[4] Berzelius, Tr. de Chim. 4. p. 274.

[5] Brandenberg. Gmelin's Handb. 6. p. 171.

[6] N. W. Fischer. Das Verhältniss der chem. Verwandtschaft. 1830. p. 112.

[7] Fischer, op. cit. The report of Keir's experiments on the action of various metals on aqueous solutions of nitrate of silver, under different conditions, is well worth reading: it will be found in the Phil. Trans., May 30, 1790. 80. pp. 359–384.

[8] Fischer, op. cit. p. 118.

[9] Chem. Gaz. 1854. 12. p. 49.

[1] H. Rose, Bericht. d. Akadem. d. Wiss. zu Berlin, 1857. p. 311. In the translation in the Chemical Gazette of this passage there is an obvious error.

Wetzlar asserts that silver can never be so completely precipitated from the neutral aqueous solution of its nitrate by ferrous sulphate, that the subsequent addition of chloride of sodium to the solution will not cause strong turbidity.[2]

According to H. Rose, ferrous sulphate throws down the whole of the silver in a metallic state from a solution of nitrate of silver; but when a solution of nitrate of silver is mixed with one of ferrous chloride, only chloride of silver is thrown down without any metallic silver.[3] We owe to the same chemist the following additional observations on the action of ferrous sulphate on nitrate of silver:—When the ferric oxide, which is in this case formed, cannot combine with sulphuric and nitric acids, the result differs from that above stated. Thus, if moist oxide of silver be added in sufficient quantity to a solution of ferrous sulphate, the former becomes deep-black, but is still converted into metallic silver after some time, and only acquires greater stability when the quantity of oxide of silver is very predominant: the filtered liquid then contains no iron, but only sulphate of silver. The black compound is obtained most readily and of the greatest stability, when a solution of nitrate of silver is mixed with so much ammonia that the small quantity of oxide of silver separated is redissolved, and an excess of this solution is dropped into a solution of ferrous sulphate. A deep-black precipitate is then formed immediately, which has so remarkably strong a colouring power that the smallest quantity of ferrous or argentic oxide may be thereby detected. In the first case, the slightly ammoniacal solution of oxide of silver is as sensitive a reagent as the solutions of ferrocyanide of potassium and sulphide of ammonium. The black precipitate is very stable, and undergoes no change in the air. At a dull red-heat it only loses water, but is not otherwise changed in composition; at a stronger red-heat it is converted into metallic silver and ferric oxide. By trituration in an agate mortar, it acquires a metallic lustre. By dilute hydrochloric acid, it is changed into chloride of silver, metallic silver, and ferric chloride; but the quantity of metallic silver separated is not very considerable: it is greater when the substance is treated with dilute acetic acid. By nitric acid, ferric oxide is first separated, whilst silver dissolves with evolution of gas; complete solution takes place on the application of heat. When treated with a solution of perchloride of gold, chloride of silver is formed and metallic gold separated. The compound when variously prepared has the same composition: it consists of

$$AgO + 2FeO + Fe^2O^3\ [Ag^2O + 2FeO + Fe^2O^3],$$

the ferric oxide acting as an acid towards the two bases. A compound of $AgO + Fe^2O^3\ [Ag^2O + Fe^2O^3]$, without ferrous oxide, may be obtained by dissolving oxide of silver in ammonia-water and adding thereto a solution of ferrous sulphate, the former solution

[2] Schweigger's Jahrbuch der Chemie und Physik, 1828. 23. p. 94.

[3] Chemical Gazette, 1847. 5. p. 2.

being in great excess. When ferous and argentic oxides are combined with weak acids, the solutions of these neutral compounds form the black precipitate of argentic oxide, without the addition of ammonia or any other base. If ferrous and argentic acetates be used, the black compound is immediately produced, but under the influence of the free acids becomes white of itself in course of time, changing into metallic silver. A far greater quantity of the compound of oxide of silver is, however, produced when the free acids are saturated by a small quantity of a base.[4]

When a solution of sulphate of manganese (manganous sulphate) is added to a solution of nitrate of silver, there is no decomposition, or it is not until after a long time that a slight black precipitate is formed.[5]

According to R. Schneider, the reaction shown in the following equation occurs when cuprous sulphide is put into a solution of nitrate of silver:[6]—

$$Cu^2S + 2(AgO,NO^5) = 2(CuO,NO^5) + AgS + Ag.$$
$$[Cu^2S + 4AgNO^3 = 2CuN^2O^6 + Ag^2S + 2Ag.]$$

In the process of separating gold from silver by nitric acid, in former times extensively practised, a solution of nitrate of silver was obtained, from which the metal was thrown down in the metallic state by copper.

The action of stannous chloride on nitrate of silver has been previously noticed (see p. 92).

According to H. Rose, a solution of nitrate of silver produces in a solution of stannous sulphate a precipitate, which at first is whitish, but soon becomes black or brown-black, and retains this colour on boiling. By heating this precipitate (the nature of which is not stated) with hydrochloric acid, it is changed into metallic silver.[7]

The following process is recommended by Dr. Wicke for obtaining pure silver from a solution of nitrate of silver and copper:[8]—The excess of acid is to be removed by evaporation, the solution diluted with water, excess of carbonate of soda added thereto, and heat applied. The precipitated carbonates are then digested in a boiling solution of grape-sugar, when dioxide of copper (cuprous oxide) and metallic silver are thrown down. To make sure of the reduction of all the carbonate of silver, the boiling must be continued for about 10 minutes. The precipitate is filtered, and whilst still moist treated with hot solution of carbonate of ammonia, which dissolves the oxide of copper and leaves the metallic silver. The treatment by carbonate of ammonia is continued so long as the solution acquires a blue colour; washing is effected by decantation. The process is said to be simple and to take but little time. Instead of carbonate of

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[4] Chemical Gazette, 1857. 15. p. 344.
[5] Jahresber. 1857. p. 253.
[6] Idem, 1874. p. 276.
[7] Ausführliches Handbuch der analytcishen Chemie, 1851. 1. p. 243.
[8] Liebig's Annalen, April 1856, p. 143, quoted in the Chemical Gazette, 1856. 14. p. 211.

soda, potash may be used, which throws down oxides of both metals; the oxides are boiled in the grape-sugar solution, whereby the cupric oxide is reduced to cuprous oxide, and the oxide of silver reduced to the metallic state. By the addition of an ammoniacal solution of cuprous chloride to a solution of nitrate of silver, pure metallic silver is precipitated in an extremely fine state of division; it is amorphous, dull grey, and occasionally almost white.[9]

According to Naquet, when chlorine gas is passed into an aqueous solution of nitrate of silver, chloride of silver and hypochlorous acid are formed.[1] When calomel or mercurous chloride is boiled with a solution of nitrate of silver, chloride of silver and sub-nitrate of mercury (mercurous nitrate) are produced; the former salt is not soluble in a solution of the latter: the reaction is shown in the following equation:[2]—

$$Hg^2Cl + AgO,NO^5 = Hg^2O,NO^5 + AgCl.$$
$$[Hg^2Cl^2 + 2AgNO^6 = Hg^2N^2O^6 + 2AgCl.]$$

H. Sainte-Claire Deville discovered that when perfectly dry chlorine gas is passed over dry nitrate of silver, kept constantly heated to from 55° C. to 60° C., anhydrous nitric acid and chloride of silver are formed, and oxygen gas is evolved.[3]

If phosphorus is kept immersed in an aqueous solution of nitrate of silver, there is reduction of silver to the metallic state. This fact is applied in electroplating, when it is desired to coat an article with a conducting film. The article is first dipped for a moment into bisulphide of carbon, containing $\frac{1}{12}$ of its weight of phosphorus in solution, whereby, on its withdrawal, phosphorus is deposited in a state of fine division over its surface as the bisulphide evaporates, and it is then dipped into an aqueous solution of nitrate of silver, from which silver is reduced by the coating of phosphorus. The surface of the article before immersion in the solution of phosphorus should be perfectly free from water. In this manner, the most delicate objects, such as lace, feathers, insects, and fruit, indeed any which will bear immersion in a liquid, may be coated with a film of silver.[4]

When a piece of common charcoal remains for a long while in an aqueous solution of nitrate of silver, its surface becomes studded with bright spangles of metallic silver. Reduction in this case is probably due to the hydrogen in the charcoal; for when charcoal which has been strongly heated is used, there is but slight separation of silver.

Two experiments on this subject have been made in my laboratory: in one experiment (A) a stick of common wood-charcoal was immersed in a solution of 50 grains of crystallized nitrate of silver in

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[1] Millon and Commaille, Jahresber. 1863. p. 283.
[2] Jahresber. 1860. p. 201.
[3] Field, Journ. of the Chem. Soc. 1858. 10. p. 242.
[4] Ann. de Chim. et de Phys. 3. s. 28. p. 241.
[9] See an excellent work entitled, A Manual of Electro-Metallurgy, by George Shaw. 2nd ed. Birmingham, 1844. p. 91.

8 fluid ounces of water, while in the other experiment (B) a stick of the same kind of charcoal, which had been very strongly heated, was immersed in another similar solution; and both solutions were contained in stoppered bottles. The experiments were begun on August 9th, 1859. In (A), metallic silver was soon deposited on the charcoal, and continued to increase; whereas in (B), it was not until after the lapse of several months that any metallic silver was observed on the charcoal. In June 1876 the charcoal in (A) had a very beautiful appearance, silver in exceedingly thin, comparatively large flakes, and of bright metallic lustre, hanging from the surface of the charcoal from top to bottom; but in (B) the surface of the charcoal presented only here and there small, bright, apparently crystalline particles of silver. Assuming the reduction of the silver to have been due to hydrogen, the difference between the results in the two experiments may be explained by the fact that common charcoal, produced by carbonization at a comparatively low temperature, contains much more hydrogen than charcoal which has been exposed to a very high temperature.

Concerning the action of charcoal on solutions of various metals, Lazowski remarks that "the parts of the charcoal, upon which certain metals are deposited in preference, are the extremities; whilst other metals cover equally all the surface of the reducing body; at other times, and this occurs with the protochloride of tin, the metal appears in very brilliant crystals, disseminated on the periphery of the charcoal."[5] Light, possibly, may affect this action.

Mrs. Fulhame dipped pieces of silk in a weak aqueous solution of nitrate of silver, and while wet exposed them to the action of hydrogen gas in the dark. In one experiment, she writes, "I soon observed evident signs of reduction; the white colour of the silk was changed to a brown, which became gradually more intense; and the surface of the silk, opposed to the gas, was coated with reduced silver: various colours, as blue, purple, red, orange, and yellow, attended the reduction. These colours often change, and are succeeded by others in the progress of the reduction. The threads of the silk look like silver wire, tarnished in some parts, but of great lustre in others. These experiments on the reduction of gold and silver, were often repeated with nearly the same result."[6]

There is not a little disagreement amongst chemists concerning the action of hydrogen on a solution of nitrate of silver, as will appear from the following statements on the subject. According to Brunner, when pure hydrogen is passed through an aqueous solution of nitrate of silver during several hours, a light grey precipitate of metallic silver is formed; but after continuing the operation during a week, the greater part of the salt remained unchanged.[7] B. Renault, on the contrary, states that the reducing action of hydrogen on salts

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[5] Chemical Gazette, 1848. 6. p. 43.

[6] An Essay on Combustion, with a view to a new Art of Dying (*sic*) and Painting. By Mrs. Fulhame. London, 1794. p. 21.

[7] Jahresber. 1864. p. 124.

of silver, which he had observed, was due to the impregnation of the hydrogen with small quantities of antimoniuretted, arseniuretted, siliciuretted, or phosphuretted hydrogen.[8] According to Russell, when pure hydrogen is passed through a concentrated solution of nitrate of silver, there seems at first to be no action; but after the lapse of about half an hour, metallic silver is precipitated, which, as the reaction proceeds, acts upon the nitric acid set free and forms nitrite of silver. This latter salt is not decomposed by hydrogen, so that the final result is the complete conversion of the nitrate of silver into nitrite. From very diluted solutions of nitrate of silver, on the contrary, silver is separated by hydrogen in the metallic state, since very diluted nitric acid, containing not more than 7% of free acid, is without, or nearly without, action on silver.[9] H. Pellet asserts that hydrogen — prepared with distilled [re-distilled?] zinc and pure hydrochloric acid, and passed successively through solutions of caustic soda and nitrate of silver—has no action, at ordinary temperatures, on a neutral solution of nitrate of silver, containing 30 grammes to 1 litre. At 80° C. there is produced, but only momentarily at the first introduction of the hydrogen, a light grey-yellow precipitate; and after filtration, the filtrate undergoes no further change. A solution of fused nitrate of silver, which on account of the oxide of silver formed by fusion has always a somewhat alkaline reaction, is, whether cold or hot, attacked by pure hydrogen only to the extent of the reduction of the oxide of silver dissolved. But if the solution be acidulated with nitric acid, no precipitate is formed in the solution whether cold or hot. Pellet contradicts the statement of Russell with regard to the formation of nitrite of silver, and maintains that in the presence of nitric acid, especially in a hot solution, that salt cannot exist.[1] N. Békétoff contradicts Pellet, and found reduction of silver to take place when pure hydrogen is passed into a neutral solution of nitrate of silver, but only when the operation is continued for a very long time; and that the quantity of silver separated is exactly proportional to the quantity of hydrogen absorbed. He bases his statements on quantitative determinations.[2]

If coal-gas is passed through a neutral aqueous solution of nitrate of silver, the latter becomes turbid, and a substance is deposited, which in a dry state detonates violently when heated or struck with a hammer. It consists of microscopic prismatic crystals. By the action of hydrochloric acid, it evolves a combustible gas of high illuminating power, which, on being passed into an aqueous solution of nitrate of silver, throws down a micro-crystalline substance, highly explosive when dry, and yielding from 78·3% to 84·0% of silver. In a strongly acidulated solution of nitrate of silver, coal-gas also produces a precipitate, but much less in quantity.[3] This is, doubtless,

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[8] Jahresber. 1873. p. 289. Compt. rend. 76. p. 384.
[9] Jahresber. 1874. p. 289.
[1] Idem, p. 290.
[2] Idem, p. 290.
[3] A. Vogel, jun., and C. Reischauer, Jahresber. 1858. p. 208.

the so-called acetylide of silver, or the argentacetyloxide of Berthelot, of which the formula is C^4Ag^2HO [$(C^2Ag^2H)^2O$].[4]

Berzelius directs attention to the antiseptic power of nitrate of silver, and states that water containing $\frac{1}{120000}$ of the salt by weight, is preserved from change. He suggests that a little hydrochloric acid might be added in order to precipitate the silver as chloride and render the water potable.[5]

According to H. Rose, an aqueous solution of nitrate of potash or soda, containing sufficient nitrate of silver, yields crystals, of the same form as those of nitre, which are composed of the alkaline and silver salt. In this way he produced crystals of the formula $AgO,NO^5 + 3(KO,NO^5)$ [$AgNO^3 + 3KNO^3$]. From a solution of nitrate of soda and nitrate of silver in excess, rhombic crystals of the latter salt separated at first, and then crystals of the form of nitrate of soda, which varied in composition, containing, for 1 equivalent of nitrate of silver, from 2 to 4·2 equivalents of nitrate of soda.[6]

By heating an aqueous solution of sulphurous acid with nitrate of silver to 200° C. in a closed tube, Geitner obtained microscopic crystals of sulphide of silver, resembling the native sulphide; and a similar result occurred when metallic silver was substituted for the nitrate.[7]

According to J. Myers, when crystals of nitrate of silver are exposed to the action of a solution of sulphide of potassium, they acquire a thin coating of sulphide of silver, underneath which is an extremely thin film of metallic silver.[8]

Double nitrate of silver and ammonia. Argento-nitrate of ammonia. $AgO,NO^5 + 2NH^3$ [$AgNO^3 + 2NH^3$].—It is obtained in bright rhombic prisms by evaporating a solution of nitrate of silver in excess of ammonia-water in the dark: when fused, say in a glass vessel, it is resolved into ammonia, nitrogen, nitrate of ammonia, and metallic silver, which is deposited on the surface of the glass in the form of a brilliant metallic coating. Kane expresses the reaction as follows:—

$$3(AgNH^3 + NH^3,HO,NO^5) = 3Ag + 2NH^3 + N + 3(NH^3,HO,NO^5).$$
$$[3(NH^2Ag + N^2H^4O^2) = 3Ag + 2NH^3 + N + 3N^2H^4O^2.]$$

At a higher temperature, the nitrate of ammonia is decomposed, and nitrous oxide is evolved.[9] This salt is very soluble in water, and in the dark is permanent in the air, but blackens on exposure to light, with the disengagement of ammonia; heated to 100° C. it suffers no loss in weight. Dry nitrate of silver absorbs ammonia, and the product has the formula[1] $AgO,NO^5 + 3NH^3$ [$AgNO^3 + 3NH^3$].

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[4] Jahresber. 1866. p. 512. See also observations by Professor Rudolf Böttger on the action of hydrogen on a solution of nitrate of silver and ammonia with an excess of ammonia. Chem. Gazette, 1859. 17. p. 264.

[5] Tr. de Chim. 4. p. 276.

[6] Jahresber. 1859. p. 230; and 1857. p. 255.

[7] Idem, 1864. p. 142.

[8] Idem, 1873. p. 244.

[9] Kane's Elements of Chemistry, 1841. p. 834.

[1] Berzelius, Tr. de Chim. 4. p. 277. Gmelin's Handb. 6. p. 177. Marignac, Jahresber. 1857. p. 256.

Nitrate of silver, and chloride, bromide, iodide, and cyanide of silver.—No compound of nitrate and chloride of silver can be formed, either in the wet or dry way. By heating a mixture of one equivalent of nitrate and one of bromide of silver to 182° C. combination takes place, and the product, on solidifying, becomes a crystalline mass. A concentrated solution of nitrate of silver dissolves iodide of silver in notable quantity: thus 100 parts by weight of a solution, saturated at 11° C., dissolves in the cold 2·3, and when boiling 12·2 parts of iodide of silver. By heating a moderately concentrated solution of nitrate of silver, containing an excess of acid, with iodide of silver, a yellow, oily liquid separates, which solidifies to a crystalline mass; by longer boiling this mass with nitrate of silver and nitric acid, a crystalline compound of nitrate and iodide of silver is formed, consisting of one equivalent of each: it melts at 94° C., and is hardly changed by exposure to light. By dissolving iodide of silver in a boiling concentrated solution of nitrate of silver, acicular crystals of a pearly lustre are deposited on cooling, which consist of two equivalents of nitrate and one of iodide of silver. Combination occurs when nitrate and iodide of silver are heated together. A double salt, consisting of one equivalent of nitrate and two of cyanide of silver, is obtained when freshly-precipitated cyanide of silver is dissolved in a boiling concentrated solution of nitrate of silver: on slow cooling of the solution, this salt is deposited in fine, very brilliant, acicular crystals; it is decomposed by water, and when heated melts, and then detonates powerfully, silver containing cyanogen being left.[2]

Nitrite of Silver, AgO,NO^3 [$AgNO^2$].

The formation of this salt by heating nitrate of silver has been described. It may be otherwise prepared by adding an aqueous solution of a nitrite, say of potash, to a similar solution of nitrate of silver, avoiding excess of the former, in which case a double nitrite would be produced. From cold solutions it is deposited in hair-like crystals, and from hot ones in colourless prisms. In small quantity it appears white, and, in large, yellowish. According to Mitscherlich, it dissolves in 120 parts by weight of water, at 15° C., and according to Fischer in 300. It is more soluble in hot water, and is insoluble in alcohol.[3]

Supposed basic nitrite of silver.—It was discovered by Proust, but its composition has not been ascertained. It is formed when silver in powder is boiled during a considerable time with a neutral aqueous solution of nitrate of silver. A bright yellow solution of the salt is thus obtained, which does not crystallize even when evaporated to the sp. gr. of 2·4; and when evaporation is carried further a saline mass is the product. Water, it is stated, resolves this mass into neutral

[2] Handwörterbuch der Chemie, 1859. 7. pp. 171, 172.
[3] Berzelius, Tr. de Chim. 4. p. 278. Gmelin's Handb. 6. p. 169. Handwörterbuch der Chemie, 7. p. 194. Storer's Dict. of Solubilities, p. 400.

nitrite, which dissolves, and into a more basic nitrite, which is left in the state of a yellow insoluble powder. The neutral salt may also be prepared by neutralizing the sub-salt with hydrochloric acid and filtering the solution of it from the resulting chloride of silver. On exposure to the air, the nitrite is changed into nitrate of silver. A solution of the basic nitrite causes a blue deposit in tincture of litmus, the solution becoming neutral; a violet coloration in tincture of cochineal, whereas that from the nitrate is scarlet; and it decolorizes a solution of indigo in sulphuric acid, silver being reduced. Caustic ammonia throws down metallic silver from the solution, and afterwards there is no nitrous acid in the liquid, but only nitric acid, ammonia, and oxide of silver which is dissolved by the excess of ammonia. When a few drops of the solution of subnitrite are poured into boiling water, it becomes yellow, red, and black in succession, and the nitrous is changed into nitric acid at the expense of the oxygen of the oxide of silver.[4]

Double nitrite of silver and potash, $AgO,NO^3 + KO,NO^3 + HO$ [$AgNO^2 + KNO^2 + H^2O$].—This salt crystallizes in yellow prisms, like those of nitre, from a concentrated aqueous solution of nitrite of potash, saturated with nitrite of silver, at 60° or 70° C. It is permanent in the air, and dissolves in a small quantity of water, but is resolved into its component salts by a large quantity.[5]

Supposed compound of nitrate and nitrite of silver.—Divers has published the results of some experiments upon the action of heat on nitrite of silver, and suggests that in this manner he obtained a compound of nitrite with nitrate of silver; yet he admits that the evidence of its existence is but slender.[6] Divers has also described a salt of nitrous oxide, NO [N^2O], having the formula AgO,NO [AgNO].[7]

Silver Compound said to be analogous to Purple of Cassius.

This compound, according to H. Schulz, is produced by stirring hydrated protoxide of tin (stannous hydrate) with the addition of water so as to form a thin milky liquid, adding thereto a neutral solution of nitrate of silver, and gently heating the mixture. There is thus formed a dark-brown substance of which the composition, after drying at 100° C., is shown in the following formula:[8]—

$$Ag^2O,SnO + 3SnO^2 + 3HO.$$
$$[Ag^4SnO^2 + 3SnO^2 + 3H^2O.]$$

In repeating this experiment in my laboratory, the compound was found to be purplish-brown (H. Louis, 1876).

It should be stated that the purple of Cassius, about the nature of which there has been so much discussion, seems to be nothing more than peroxide of tin or stannic acid, in intimate mixture with gold in

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[4] Berzelius, Tr. de Chim. 4. p. 278.
[5] Jahresber. 1863. p. 164; 1862. p. 102.
[6] Journ. Chem. Soc. 1871. new ser. 9. p. 85.
[7] Proc. Roy. Soc. 1871. 19. p. 425.
[8] Inaugural-Dissertation über eine dem Goldpurpur analoge Silberverbindung. Göttingen, 1857.

an extremely fine state of division; or to be, in fact, a kind of lake of which the base is peroxide of tin and the colouring matter metallic gold. Debray has adopted this view, of which the priority is however claimed for Fischer, who published a paper on the subject several years previously.[2] But with better reason it might have been claimed for Faraday, who, in his beautiful paper on the "Experimental Relations of Gold (and other Metals) to Light," communicated to the Royal Society, November 15, 1856, clearly proposed the same view. His words are, "I believe the purple of Cassius to be essentially finely-divided gold, associated with more or less of oxide of tin."[1] The experimental evidence which he presents in support of this opinion conclusively, in my judgment, establishes its correctness. It may possibly be found that the so-called silver purple is nothing more than an intimate mixture of stannic oxide and metallic silver in an extremely fine state of division.

SILVER AND CARBON.

Gay-Lussac has been repeatedly cited as the authority for the statement, that carbon and silver combine at the melting-point of the latter. In 1835, that accurate chemist published a short paper on assaying argentiferous matters by the *wet way*, which contains the following record:—"I have sought to detect the presence of mercury in silver, by heating 1 gramme of it in a muffle, in a small crucible, with lamp-black, in order to avoid the vaporization of the silver; but I have been deceived in my attempt; after three-quarters of an hour's heating, the weight of the silver had very sensibly increased. In one experiment, the excess of weight had risen to more than 30 milligrammes (*i.e.* 3% of the silver)."[2] I am not aware that Gay-Lussac communicated any further information on the subject in question. There is no mention of any analysis of the silver after this treatment. Now, the lamp-black of commerce is often, if not generally, exceedingly impure and contains sulphur, on which account we were long ago compelled in the metallurgical laboratory to abandon its use as a lining for crucibles. The increase in weight may have been, and probably was, due to sulphur and not to carbon; and, in the absence of positive evidence to the contrary, the inference that it was due to carbon is a mere assumption. There is certainly no satisfactory evidence in proof of the *direct* combination of carbon with silver by heat. On the contrary, those who have had experience in the metallurgical processes connected with silver, know that there is not the least ground for suspecting that silver can take up even the smallest quantity of carbon under the circumstances.

Berzelius heated pyro-racemate of silver, and obtained a grey metallic powder, which looked exactly like metallic silver, and

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[1] Jahresber. 1872. p. 275; and 1866. p. 265.
[1] Phil. Trans. 1857. p. 170.
[2] Ann. de Chim. et de Phys. 1835. 58. p. 218.

acquired a metallic lustre when burnished.[3] Heated to redness in an open crucible, this powder yielded a residue of dull white silver, from the weight of which, it was inferred that the powder above-mentioned had the formula AgC^2 [AgC]. In another experiment, the residue, obtained by heating the silver salt in a small tube, was grey and metallic in lustre, and corresponded more nearly to the formula Ag^2C^3 [Ag^4C^6] than to AgC^2 [AgC].

Regnault heated malate of silver to 150° C., when a slight explosion occurred, and there was left a dark grey substance, very homogeneous, and decidedly metallic in lustre, which, by the action of nitric acid, yielded a flocculent residue.[4] "From this," writes Regnault, "the residue [*i.e.* the dark grey substance] can be nothing else than carburet of silver;" and, from the weight of the metallic silver which he found it to contain, he assigned to it the formula AgC^2 [AgC].

Redtenbacher and Liebig procured what they believed to be carbide of silver from cyanide of silver. This salt was heated, when it melted without at first evolving gas, but at a higher temperature cyanogen was disengaged and dicyanide of silver, Ag^2Cy [idem], formed: at a certain stage there was incandescence and nitrogen was liberated, and there was left "a dull white melted carbide of silver," from which prolonged calcination did not separate carbon. The carbide was heated with access of air, when the carbon burnt at its surface, and a layer of pure silver remained, which protected the underlying carbide from oxidation. On dissolving the carbide in dilute nitric acid, a network of pure carbon was left.[5] No analysis is given nor is any formula proposed.

According to Gerhardt and Cahours cuminate of silver yields, when heated, a dull, yellow, earthy residue of the formula AgC [Ag^2C], from which nitric acid extracts the silver.[6]

Carbonate of Silver, AgO,CO^2 [Ag^2CO^3].

It is a pale yellow powder, of sp. gr. 6·0 at 17·5° C., and dissolves in 31,978 parts of water at 15° C.[7] and in 961 parts of water saturated with carbonic acid.[8] It dissolves in an aqueous solution of ammonia, carbonate of ammonia, hyposulphite of soda, or cyanide of potassium. It is completely reduced by heat, and darkens on exposure to sunlight. It may be prepared by the addition of an aqueous solution of carbonate of soda to a similar solution of nitrate of silver, when it is precipitated as a white powder, which becomes yellow by the aggregation of its particles, an effect immediately produced by the application of heat.[9] H. Vogel obtained carbonate of silver in minute

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[3] Destillationsproducte der Traubensäure. Annal. der Physik und Chemie, 1835. 36. p. 28.

[4] Ann. de Chim. et de Phys. 1832. 62. p. 215.

[5] Annal. der Chemie u. Pharmacie, 1841. 37. p. 129.

[6] Berzelius, Tr. de Chim. 2. p. 484.

[7] Kremers. Storer's Dictionary of Solubilities, 1864. p. 116. Jahresber. 1852. p. 423.

[8] Lassaigne. Berzelius' Jahres-Ber. 1850. 29. p. 132.

[9] Berzelius, Tr. de Chim. 4. p. 282.

needle-shaped crystals of a lemon-colour: they were deposited from the solution described at p. 10, after it had ceased to yield crystalline protoxide of silver.[1] H. Rose observes that "it is remarkable that oxide of silver exhibits considerable affinity for carbonic acid, but none whatever for water. When the solution of an equivalent of a neutral salt of silver is decomposed by an equivalent of a neutral alkaline carbonate, neutral carbonate of silver without water is obtained, whether the solutions used be concentrated or dilute, cold or hot. Only with a large excess of alkaline carbonate is a basic carbonate of silver of the formula $3AgO,2CO^2$ [$Ag^6C^2O^7$] produced by boiling. Carbonate of silver parts with its carbonic acid at 200° C., and is converted into pure oxide of silver, which begins to lose oxygen at 250° C."[2]

SILVER AND SILICON.

According to Berzelius, it is very easy to combine silver with a small quantity of silicon by melting the two together;[3] and when a mixture of silica, charcoal-powder, and finely-divided silver is strongly heated in a crucible under a layer of glass, containing only alkaline or earthy bases, such as plate- or crown-glass, a button of silver is obtained, which, on solution in nitric acid, yields gelatinous flocculi of silica.[4] Stromeyer states, that under these conditions silver acquires both silicon and carbon. Berzelius also announced that a malleable alloy is produced by heating silver with silicon before the blowpipe.[5] But I find that there is no sign of combination when crystallized silicon is so heated in contact with silver.

The following experiments, made in my laboratory by E. Jackson (1875), have not confirmed the preceding statements of Berzelius and Stromeyer; and it is, therefore, necessary to report precisely how those experiments were made. 50 grains of very finely divided silver, prepared by precipitation with sulphite of soda, were mixed with its own bulk of powdered charcoal and an equal bulk of silica in the form of sand. The mixture was put into a small clay crucible, and the mouth of the latter then closed with a plug of charcoal. The small crucible was placed in a larger one, and the space between the two crucibles was filled up with burnt fire-clay, and the mouth of the outer crucible luted over with fire-clay. The crucibles were exposed to a high temperature in an air-furnace during two hours, then taken out and left to become cold, after which they were broken. The silver was found to be diffused in such fine particles through the mixture of charcoal and silica, that it was necessary to separate these by washing, or, as it is technically termed in Cornwall, "vanning." The silver was digested with dilute nitric acid, and the solution evaporated to dryness. The dry residue dissolved wholly in dilute nitric acid, as would not have been the case if the silver had contained silicon. Another similar experiment was

[1] Jahresber. 1862. p. 228.
[2] Chemical Gazette, 1852. 10. p. 181.
[3] Tr. de Chim. 1831. 3. p. 96.
[4] Tr. de Chim. 1846. 2. p. 481.
[5] Gmelin's Handb. 6. p. 182.

made, in which granulated silver was used. The crucibles were heated during three hours in an air-furnace, of which the temperature was high enough to melt iron with facility. No trace of silicon could be detected in the silver. In a third experiment, a mixture of 10 grains of finely-divided metallic silver and 2 grains of crystallized silicon (prepared in the usual manner by heating together silico-fluoride of potassium, zinc, and sodium) was heated in a covered clay crucible. When cold the crucible was broken open, and the silicon, apparently unchanged, was found in admixture with shots of silver. By treatment with nitric acid in the manner above described, the silver was proved to be free from silicon. In the fourth experiment an attempt was made to combine silver with silicon by heating silico-fluoride of potassium with sodium and silver instead of zinc. The quantities used were as follow :—

	Grains.
Silico-fluoride of potassium	300
Sodium	80
Silver	145

A button of metal was thus obtained, which was crystalline and very brittle. On digesting a portion of it with dilute nitric acid, crystallized silicon was left undissolved, but the crystals were very much smaller than those which are formed in the usual process with zinc. The composition of the metal was found to be as follows:

	Per cent.
Silver	92·04
Silicon	2·77
Lead	4·90
Aluminium	0·15
	99·86

The lead was derived from the silico-fluoride of potassium, in which it was present as an impurity, and which I had received from a chemical manufacturer, who had prepared the salt in considerable quantity, and used leaden vessels for the purpose.

Supposed silicate of silver.—It is well known that certain compounds of silver impart a yellow colour to glass when heated in contact with it; and glass-stainers have long applied this fact in the practice of their art. But metallic silver in a finely-divided state is also capable of staining glass yellow by heat. It is conjectured that the colour is due to the formation of a yellow silicate of silver. Stas has endeavoured to ascertain whether oxygen is absorbed when the colour proceeds from metallic silver. He heated an intimate mixture of 100 grammes of very refractory glass in fine powder and 30 grammes of precipitated metallic silver, in a long tube of refractory glass, through which a current of pure dry air was kept passing. Several experiments of this kind were made at different temperatures. The conclusion at which Stas arrived is, that silver, in contact with even very refractory glass, absorbs

oxygen, and forms silicate of silver; but there is no such absorption below the temperature at which the glass softens. The tube with its contents, after this alleged absorption of oxygen, weighed 289·6545 grammes, and before 0·0308-gramme less. In this experiment the tube was enclosed in a sheet-iron sheath, and was supported in the middle on a bed of pure magnesia, previously heated before the oxy-hydrogen blowpipe: after the lapse of 20 minutes the tube collapsed and bent, so as completely to stop the current of air through it.[6] Under such circumstances, it seems possible that the increase of weight may have been due, in part at least, to other causes than the absorption of oxygen. May it not be that the yellow colour imparted by silver to glass is due to the diffusion of metallic silver in an extremely fine state of division, just as metallic gold has, in an extremely fine state of division, been proved by Faraday to be the cause of the ruby-red colour in glass coloured by gold? It has been previously stated (p. 6) that light transmitted by silver leaf of a certain thickness is yellow.

Staining Glass.—The process of staining glass yellow, which I have often seen practised in Birmingham, was thus conducted. A mixture of colcothar and precipitated chloride of silver was triturated with water to the consistency of paint. The glass was coated on one side with this mixture, and, after the latter had been gradually dried, was exposed for some time to a red-heat in a large cast-iron muffle. When cold, the colcothar was washed off. Some kinds of window-glass acquire a deeper stain than others by this treatment, which I have heard ascribed to the presence of alumina in the glass; but I have no evidence on the subject other than hearsay.

The following directions for staining glass with silver, which seem to me to possess considerable interest, were communicated to the Society of Arts in 1817 by Mr. Robert Wynn, of London, who practised the art, and were published in the Transactions of that Society. Three kinds of colour may be produced, namely, yellow, orange, and red. The preparations of silver used are as under:—

I. Chloride of silver, made by adding a solution of common salt to a solution of nitrate of silver, well washing the precipitate with hot water, and then drying it.

II. Carbonate of silver, made by adding a solution of carbonate of soda or potash to a solution of nitrate of silver, washing and drying the precipitate.

III. Phosphate of silver, made by adding a solution of common phosphate of soda to a solution of nitrate of silver, washing and drying the yellow precipitate.

IV. Metallic silver in admixture with sulphide of silver, prepared by heating silver, rolled out into thin plates, with sulphur. When the crucible has been a short time on the fire, the sulphur will first melt and then gradually burn away with a

[6] Nouvelles Recherches sur les Lois des Proportions chimiques, etc. 1865. p. 176.

blue flame. When the flame has ceased more sulphur is to be added, and the heating continued, as before, until the blue flame disappears. The product is then taken out of the crucible and heated to redness in a muffle: it will now be white and very brittle, and is to be reduced to powder in a mortar, after which it is ready for use.

V. Metallic silver, made by immersing a stick of metallic tin in a dilute solution of nitrate of silver and warming a little; the silver will be precipitated on the surface of the metallic tin in the form of metallic leaves, which are to be scraped off, washed in warm water, dried, and ground in a mortar.

VI. Metallic silver, made by immersing a piece of copper-plate in a solution of nitrate of silver, and proceeding precisely in the manner stated in No. V.

VII. Silver is melted in a crucible with twice its weight of "crude antimony" [*i.e.* the common sulphide], and the product is to be pulverized.

Staining yellow.—(A.) A mixture of equal weights ["part" is the word used, by which I suppose is meant part by weight] of No. II. and yellow lake. The mixture is to be ground well with oil of turpentine mixed with "the thick oil of turpentine," [or that which has absorbed oxygen from the air and become thick. These lakes are made by precipitating the colouring matter from aqueous infusions of various yellow vegetable substances, containing common alum in solution, by the addition of carbonate of soda or potash, or carbonate of lime. It is only the inorganic part of the lake that can be of use; for, assuredly, the vegetable colouring matter, which will be burnt off in the process of heating, cannot aid in the staining.]

(B.) Take of No. I. 1 part; alumina, prepared by adding carbonate of soda to a solution of alum, 3 parts; oxalate of iron, prepared by adding a solution of oxalate of potash to a solution of sulphate of iron (ferrous sulphate), 3 parts; oxide of zinc, 2 parts. No. I. is to be ground first in water with the oxide of zinc, and then with the other ingredients. This is intended for "floating" on thick.

(C.) Take of No. II. and of yellow lake equal parts. The ingredients are to be ground with thin and thick oil of turpentine, and the mixture is to be laid on very thin.

(D.) Take of No. III. and of yellow lake equal parts, and of "white clay" [*i.e.* alumina prepared as stated above under (B)] half a part. The ingredients are to be ground well with thin and thick oil of turpentine, and the mixture is to be laid on thin.

Staining orange.—(E.) Take of No. V. 1 part, and of a mixture consisting of equal parts of Venetian red and yellow ochre, washed in water, and calcined red, 2 parts. The ingredients are to be ground with thin and thick oil of turpentine, and the mixture is to be laid on thin.

(F.) Take of No. VI., and of the mixture of Venetian red and yellow ochre, equal parts. The ingredients are to be treated as stated under (E). If entire panes of glass are to be stained orange, the

proportion of ochre may be greatly increased. The depth of the tint depends in some degree on the temperature of the furnace, and on the length of time during which the glass is heated, for which, though easily learned by experience, precise rules cannot be given.

Staining red.—(G.) Take of No. IV., and of oxide of iron (made by heating iron scales [smithy scales?], quenching them in water, then reducing them to powder, and calcining the powder in a muffle), equal parts. The ingredients are to be ground with thin and thick oil of turpentine, and the mixture is to be laid on thick.

(H.) Take of No. VII. and of colcothar equal parts. The ingredients are to be ground with thin and thick oil of turpentine, and the mixture is to be laid on thick.

(K.) Take of No. VII., and of the mixture of Venetian red and yellow ochre, equal parts. The subsequent treatment is the same as stated in (H). When whole panes of glass are to be stained, the proportion of ochre or of colcothar may be much increased, and the ingredients should be ground in water.

Laying on the colour.—The pattern is drawn in Indian ink. The colour is ground as fine as possible with oil of turpentine, brought to the proper consistency by admixture with thick oil of turpentine, and a little oil of spike-lavender is added. The outline is to be entirely covered with this composition; and when the latter has become dry, the composition is removed, with the point of a stick and a knife, from such parts as are not intended to be stained: in this manner the most delicate ornaments, and most intricate designs, may be executed with exactness and precision. But if the composition is required to be applied so thickly that the outline would not be visible through it, it should be first laid on as smoothly as possible; and when it has become dry, the outline should be drawn upon it with vermilion water-colour, and the design worked out in the manner stated above. Besides the precision attained by this method of proceeding, it enables the artist to produce tints of different depths in the same design; whereas the old method of floating only communicated a uniform tint to the whole pattern. The artist should contrive to charge his furnace with pieces, the colouring composition on which is ground with the same vehicle. The pieces must be very carefully dried, and placed in the furnace when it is only moderately warm.

SILVER AND BORON.

There seems to be no information concerning the combination of boron with silver.

Borate of Silver, AgO,BO^3 [$AgBO^2$].

It is described by H. Rose as a white powder, which blackens on exposure to daylight, melts at a gentle heat, and dissolves sparingly, but without decomposition, in water. It is precipitated in white flakes on mixing a moderately strong aqueous solution of nitrate of silver with a saturated aqueous solution of borax. If the latter

solution is diluted with 30 or 40 times its weight of water and then mixed with the former, after some time turbidity occurs, and oxide of silver is gradually deposited.[7]

To the same chemist we are indebted for the following interesting observations. A dilute solution of borax acts quite differently on a solution of nitrate of silver from a concentrated solution. With the latter, white borate of silver is obtained, which dissolves completely in much water: whereas, with a dilute solution of borax, pure oxide of silver of a yellowish-brown colour is precipitated, which is not dissolved by a large quantity of water. If concentrated solutions of equivalent proportions of neutral borate of soda, $NaO,BO^3 + 8HO$ [$NaBO^2 + 4H^2O$], and nitrate of silver, be mixed together in the cold, a cheesy precipitate of a dingy yellow colour is produced. If this, after filtration, be not washed, but merely pressed between blotting-paper, it is found to consist almost wholly of neutral borate of silver, $AgO,BO^3 + HO$ [$2AgBO^2 + H^2O$], only 1 equivalent of free oxide of silver being present for every 10 equivalents of this compound; the yellowish colour of the precipitate is due to oxide of silver. But if the precipitate, after filtration, be washed with cold water, nearly all the boracic acid is extracted from the borate of silver. The washing, however, on account of the solubility of oxide of silver, cannot be continued until the wash-water becomes no longer turbid on the addition of hydrochloric acid. Only 1 equivalent of boracic acid to 6 equivalents of oxide of silver was found in the precipitate, which, during drying, absorbs carbonic acid from the atmosphere. If boiling concentrated solutions of the two salts be mixed together, a brown precipitate is immediately produced, which becomes darker in colour when the whole is kept boiling for some time. It consists only of oxide of silver, which, during drying, attracts carbonic acid.

If concentrated solutions of equivalent proportions of biborate of soda, $NaO,2BO^3 + 10HO$ [$Na^2B^4O^7 + 10H^2O$], and nitrate of silver, be mixed whilst cold, a white precipitate is produced; but much borate of silver is dissolved in the filtered liquid. When the precipitate, after filtration, was pressed, without washing, between blotting-paper, it had, according to one analysis, the composition of $3AgO,4BO^3$ [$Ag^6B^8O^{15}$]. But it varies in constitution, for some borate of silver produced in the same manner, except that it had been washed, was found to have the composition of AgO,BO^3 [$AgBO^2$]. When cold concentrated solutions of the two salts are mixed together, and the resulting white precipitate is washed with cold water, it acquires a strong brown colour on the surface, whilst internally it remains white. When it had been washed until the wash-water became free from nitric acid, it had essentially the composition of $4AgO,5BO^3$ [$Ag^8B^{10}O^{19}$]; yet it contained some soda.

If boiling concentrated solutions of the two salts be mixed, the precipitate is at first white, but soon acquires a dirty-grey colour; when not washed, but merely pressed between blotting-paper, after

[7] Gmelin's Handb. 6. p. 147.

filtration, it has the composition $AgO,BO^3 + HO$ [$2AgBO^2 + H^2O$]. But if, after mixing the boiling solutions, the whole be heated to boiling, the grey precipitate becomes brown, and then, if the boiling be continued for some time, changes to a deep blackish-brown. If the compound be washed with hot water after filtration, the wash-water will contain much borate of silver, and the residue consist of oxide of silver, which, during the washing, has absorbed carbonic acid.[8]

SILVER AND PHOSPHORUS.

Pelletier experimented on the subject in 1792, and scarcely any information of importance has been added to what he published respecting it. He dropped phosphorus on silver heated to redness in a crucible, when the metal instantly melted; and he continued to put in more until he believed the silver to be saturated with it. The metallic product, while molten, had a tranquil surface; but, on cooling, much phosphorus was emitted, and the surface became mammillated all over (*devint toute mamelonnée*). He repeated the experiment several times and with the same result. The quantity of phosphorus retained after solidification was about 15%, and it was inferred that it lost about 10% on passing from the liquid to the solid state, but the ground of that inference is not stated.[9] We have confirmed Pelletier's statement as to the evolution of phosphorus during cooling, but not as to the quantity of it retained by the solidified silver.

The following observations on this subject have been made in my laboratory by my assistant, R. Smith. To 500 grains of molten silver in a clay crucible, 200 grains of red or amorphous phosphorus were added in successive portions, and intermixture promoted by stirring well from time to time. When the burning of the vaporized phosphorus had ceased, and the surface of the liquid metallic mass had become smooth and tranquil, the crucible was taken out of the furnace, and its contents carefully watched during cooling. At first a little phosphorus vapour continued to be given off and inflame, the surface of the metallic mass remaining smooth and tranquil. But afterwards, when the evolution of phosphorus vapour had ceased, and the surface of the metal appeared to have set, there suddenly occurred a hissing spitting sound, the metallic mass rose in the crucible and continued to rise for a few seconds until it seemed to have doubled its volume, and this expansion was attended with the escape from its surface of jets of phosphorus vapour, which burned with the emission of brilliant yellowish-white light so characteristic of that element. When cold, the metallic mass appeared dead-white on the surface, and feebly lustrous. It was cut vertically through the centre, and found to be vesicular in the upper part and solid underneath. The metal forming the surface of the cavities in the upper part was yellowish-white and crystalline, while the cut surface of the lower part was white and crystalline, like pure silver. The upper and

[8] Chemical Gazette, 1853. 11. p. 232. | [9] Ann. de Chimie, 1792. 13. p. 109.

lower parts were separately submitted to chemical examination, with the following results:—*Upper part.*—It contained 0·293 per cent. of phosphorus; and by washing the cavities with water, phosphoric acid, equivalent to 0·072 of phosphorus, was dissolved out. *Lower part.*—A portion of this solid part, taken from the centre, contained 0·207 per cent. of phosphorus.

Phosphorus acts on molten lead as it does on molten silver, on which subject information will be found in a preceding volume by the Author on the Metallurgy of Lead (pp. 74, 75).

Wicke found that when a stick of phosphorus, wound round with a strip of silver, was immersed in a concentrated solution of nitrate of silver, it became coated externally in the course of some weeks with bright crystalline silver, and that the phosphorus was superficially covered with a thin layer of dark phosphide of silver, but had undergone no change inwardly.[1]

When phosphuretted hydrogen gas is passed into an aqueous solution of nitrate, sulphate, or acetate of silver, or into an ammoniacal solution of chloride of silver, a voluminous brown precipitate is formed, which is metallic silver quite free from phosphorus. On long standing this precipitate subsides, and becomes grey-white and metallic in appearance; and while still brown it immediately acquires the metallic lustre of silver by burnishing. Subsidence is much promoted by a gentle heat.[2] According to Rose, the oxygen of the oxide of the metal combines with both elements of the gas, producing phosphoric acid and water. Fresenius and Neubauer, on the contrary, state that they found the precipitate, formed by passing phosphuretted hydrogen into a neutral solution of nitrate of silver, to consist of 94·73% of silver and 5·27% of phosphorus: these numbers correspond to the formula PAg^5 [idem], which gives 94·57% of silver and 5·43% of phosphorus. But, without expressing a decided opinion as to the nature of this precipitate, they considered it probable that it might be a mixture of phosphide of silver and metallic silver, since one-third of the phosphorus introduced remained in the solution as phosphoric acid.[3] A precipitate containing phosphorus is also produced when the vapour of phosphorus is passed into a solution of nitrate of silver.

Landgrebe heated phosphate of silver,[4] of the formula $3AgO,PO^5$ [Ag^3PO^4], with $\frac{1}{2}$th of its weight of charcoal, and produced, he states, phosphide of silver, containing 33·23% of phosphorus. Reduction took place at an incipient red-heat. The product, when quite cold, was a brittle, spongy, dark-grey, easily sectile, sintered mass, which on being filed acquired the lustre of silver: its fracture had also the same lustre. By trituration it was easily reduced to a grey-white powder.[5]

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[1] Jahresber. 1852. p. 333.

[2] Ueber das Verhalten der Phosphorwasserstoffgase gegen Auflösungen von Metallen. H. Rose. Poggendorff's Ann. d. Phys. u. Chem. 1828. 14. p. 183.

[3] Jahresber. 1862. p. 229.

[4] Prepared by mixing aqueous solutions of common phosphate of soda and nitrate of protoxide of silver.

[5] Schweigger-Seidel. Jahrbuch der

The phosphates of silver have no metallurgical interest, and for information concerning them treatises on chemistry, such as Gmelin's Handbook, must be consulted.

SILVER AND ARSENIC.

Arsenide of Silver.

Our knowledge of the compounds of silver and arsenic is still very imperfect. Gehlen heated a mixture of equal parts by weight of silver in powder and metallic arsenic, and described the product as compact, brittle, steel-grey, and fine-grained. It contained 16% of arsenic, and may, therefore, be nearly represented by the formula Ag^4As [idem]. He reports that combination was unaccompanied by incandescence.[6] It was this unfortunate chemist who died from the accidental inhalation of arseinuretted hydrogen gas. Berthier ascribes the following characters to an alloy containing 14·8% of arsenic: "dark-grey, dull, brittle, acicular-crystalline in structure; by friction it acquires the lustre and colour of silver; it is very fusible, and undecomposable by heat. It may be easily prepared by melting a mixture of silver in powder, arsenious acid, and black flux."[7] Guettier states that an alloy containing 14% of arsenic is grey-white, dull, brittle, very fusible, and acquires a metallic lustre by friction.[8]

The following observations on arsenide of silver, prepared by heating the two elements together, have been made in my laboratory by my assistant, R. Smith. 500 grains of silver were melted under charcoal in a clay crucible, and 200 grains of metallic arsenic added thereto in three successive portions. The metallic mass was well stirred and left at rest for a short time until the surface became tranquil, when the crucible was taken out of the furnace and allowed to cool. Fumes of arsenic continued to escape from the product until near the point of its solidification; but not the slightest movement of its surface occurred, as in the similar experiment with phosphorus and silver. The product was hard and brittle, though somewhat tough; its fracture was granular and slightly crystalline, dark iron-grey, and dull in lustre, but by burnishing it became white and acquired a bright metallic lustre. It was composed as follows:—

	Per cent.
Silver	81·46
Arsenic	18·54

This composition corresponds to the formula Ag^3As [idem], from which the calculated composition is as under:—

	Per cent.
Silver	81·20
Arsenic	18·80

The proportion of arsenic in the product of this experiment exceeds by about 2·5 per cent. that which Gehlen found in the pro-

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[6] Chemie und Physik. 1830, 60. p. 187.
[7] Gmelin's Handb. 6. p. 186.
[7] Tr. des Ess. 2. p. 784.
[8] Op. cit. p. 151.

duct obtained by him in nearly the same manner, as above recorded.

Alloys of silver and arsenic heated in atmospheric air.—By roasting arseniuretted silver with free access of air, arsenious acid is evolved, but, according to Plattner, some arseniate of silver is formed.[9]

This subject has been carefully investigated in my laboratory by R. Smith, with the following results:—Arsenide of silver, prepared in the manner just described and found by analysis to contain 18·54 per cent. of arsenic, was the substance operated upon. Of this substance, in the state of fine powder, 84·9 grains were exposed in a scorifier in a muffle during three hours to a very low and carefully regulated temperature, described as a "dull black heat." Immediately after introducing the scorifier, the iron-grey particles of the arsenide of silver became white, and fumes of arsenious acid were evolved, but no odour of the vapour of metallic arsenic was perceived. After this treatment the product weighed 70·63 grains; it was again roasted at a somewhat higher temperature than previously until fumes ceased to be evolved, which occurred after the lapse of about an hour. The product now resembled finely-divided silver and weighed 70·25 grains, 17·26 per cent. of arsenic having been vaporized: it was next digested with dilute sulphuric acid, which was found to dissolve out a little arsenic acid, AsO^5 [As^2O^5], and protoxide of copper (cupric oxide), both of which were quantitatively estimated and amounted to 0·106 per cent. of arsenic acid and 0·153 per cent. of protoxide of copper. Now, in accordance with the formula of arseniate of copper, $3CuO,AsO^5$ [$Cu^3As^2O^8$], 0·106 of arsenic acid requires 0·112 of protoxide of copper; but there was an excess of copper amounting to 0·041. The copper was derived from the silver, which had been sent to me from silver-works where the Ziervogel and Augustin processes were carried on, and copper was used for precipitating the silver. If we suppose that the arsenic acid found was in combination with oxide of silver, according to the formula $3AgO,AsO^5$ [Ag^3AsO^4], then the product would have contained only 0·426 per cent. of arseniate of silver. After treatment with dilute sulphuric acid, the residue was dissolved in nitric acid and found to contain 0·753 per cent. of arsenic. But if arseniate of silver had existed in the residue, it would have been dissolved out by dilute sulphuric acid equally with protoxide of copper, and silver would have been found in the solution, which was not the case. Hence it may be pretty certainly inferred from the foregoing *data*, that no arseniate of silver is produced in the roasting of arsenide of silver with free access of air, or that, if any be formed in such process, it is only in very small quantity.

Sulphides of silver and arsenic heated in atmospheric air.—The following experiment on this subject was made by Plattner:—He heated proustite, $3AgS,AsS^3$ [$3Ag^2S,As^2S^3$], in fine powder on a clay scorifier in an open muffle gradually to moderate redness, stirring from time to time. It was changed, with the evolution of sulphurous acid,

[9] Die metallurgischen Röstprozesse, 1856. p. 160.

arsenious acid, and "sub-oxide of arsenic," into a somewhat loose and partially granular mass, which on cooling became brown and contained intermixed small particles of metallic silver mostly in a hair-like form. The brown powder remained unchanged when more strongly heated, and consisted mostly of arseniate of silver. When, on the contrary, during the roasting it was triturated from time to time in an iron mortar, so as to effect as complete an intermixture as possible of the sintered particles beneath with the roasted ones above, there was no separation of metallic silver; the whole of the silver being changed into arseniate of silver, which at a somewhat higher temperature seemed to remain unaltered.[1]

Sulphides of silver and arsenic heated in a current of steam—Patera found that by roasting proustite during 5 hours in a current of steam, the silver was reduced to the metallic state, and was perfectly free from arsenic.[2]

Arsenite of Silver, $2AgO,AsO^3$ [$Ag^4As^2O^5$].

On adding an aqueous solution of arsenite of potash or soda to an aqueous solution of nitrate of silver, arsenite of silver is thrown down as a yellow powder, which gradually acquires a dark-grey colour: it is insoluble in water, but soluble in nitric or acetic acid, in ammonia-water, and in an aqueous solution of potash. The potash solution, so far from yielding a precipitate on the addition of chloride of potassium, dissolves freshly-precipitated chloride of silver; but metallic silver is slowly deposited from it and arseniate of potash is formed. To Wöhler we owe the following observations on the action of a solution of caustic soda on arsenite of silver:—Heated with a concentrated solution of soda, arsenite of silver rapidly becomes black. In order to complete the action, boiling must be long continued; and the liquid poured off from the black powder,—which settles readily,—and be replaced by a fresh solution of soda: if this be not done, the powder retains arsenic. It is then well washed and dried, when it is obtained as a heavy black powder with a tinge of grey, which, by burnishing, acquires a dull metallic lustre. The decanted solution contains arseniate of soda, which sometimes separates in crystals. If the arsenic acid is precipitated by a magnesia salt and ammonia, no arsenious acid is found in the filtrate. The black substance is stated to be a mixture of silver and argentous oxide, in equal equivalents. When heated alone, it is readily changed into greyish-white metallic silver, with a loss of 2·4% of oxygen: pure argentous oxide would lose 3·56% of oxygen. Wöhler used in his experiments commercial arsenious acid for the preparation of his arsenite of silver, and the latter was found to contain antimony, although the acid had been dissolved in ammonia; and when the black substance was ignited and afterwards digested with nitric acid, white antimoniate of silver remained undissolved.[3] Arsenite of silver,

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[1] Die metallurgischen Röstprozesse, 1856. p. 90.

[2] Idem, p. 246.

[3] Chem. Gazette, 1857. 15. p. 209.

it is stated, blackens on exposure to light. When heated in a glass tube, it becomes black at a certain temperature; and at a stronger heat, arsenious acid sublimes, and the residue consists of a mixture of metallic silver and arseniate of silver.[4]

Arseniate of Silver, $3AgO,AsO^5$ [Ag^3AsO^4].

It is precipitated as a dark brown-red powder when an aqueous solution of arsenic acid or of arseniate of potash, soda, or ammonia is added to an aqueous solution of nitrate of silver. When heated, it melts into a dark brown-red glass. It is decomposed by hydrochloric acid with the production of chloride of silver. It is insoluble in water, but soluble in ammonia-water, aqueous solution of carbonate of ammonia, acetic acid, and by heat in aqueous solutions of sulphate, nitrate, and succinate of ammonia. By keeping melted 1 equivalent of hydrated arsenic acid with 2 equivalents of nitrate of silver, until all the nitric acid is driven off, a yellow, nearly transparent, glass is formed, which is decomposed by water, the undissolved residue consisting of a brown basic salt. When a mixture of silver and arsenic acid is heated to fusion, the former dissolves with the disengagement of arsenious acid, and the product is a colourless glass, which contains an excess of acid, and from which water dissolves arsenic acid, leaving insoluble brown arseniate of silver. At a high temperature, arseniate of silver yields oxygen, arsenious acid, and arsenide of silver.[5]

SILVER AND ANTIMONY.

Antimonide of Silver.

Alloys of these metals are obtained by heating them together; and they are here described, because it is desirable to know what reactions occur in certain metallurgical processes in which antimonial silver ores are treated. And for the same reason the subject of "Silver and Arsenic" has just been considered. The information which Berthier communicates respecting these alloys is as follows:—"Antimony and silver have much affinity for each other, and combine together in all proportions. Their whiteness decreases as the proportion of antimony increases: they are always brittle, and only a very small quantity of antimony suffices to impart that quality to silver (*pour aigrir l'argent*). The antimonide, consisting of 54·5 per cent. of antimony and 45·5 per cent. of silver (*i.e.* nearly in the ratio of one atom of antimony to one of silver), is very brittle, lamellar, like regulus of antimony (*i.e.* metallic antimony), but more grey. The antimonides of silver are very fusible, and wholly decomposed

[4] Chem. Gazette, 1857. 15. p. 219. Handwörterbuch der Chemie. Supplement, p. 366. Gmelin's Handb. 6. p. 186.

[5] Handwörterbuch der Chemie. Supplement, p. 379. Gmelin's Handb. 6. p. 187. Berzelius, Tr. de Chim. 4. p. 293.

by cupellation or by fusion with nitre, pure silver remaining."[6] According to H. Rose, antimonide of silver is but imperfectly decomposed by heating it with chloride of ammonium: by repeated treatment it is most probable that metallic silver would alone remain; since the more frequently calcination is resorted to, the more the antimonide of silver decreases in weight and the residue becomes less and less brittle.[7]

The following experiments on the alloys of silver and antimony have been made in my laboratory by R. Smith. In preparing them, the silver was first melted under charcoal in a clay crucible, and the antimony then added. The metal was well stirred with a charred stick, and left in the furnace for a short time, after which the crucible was taken out and allowed to cool.

(I.) 3Ag + Sb [idem].—The quantities operated upon were 162 grains of silver and 61 grains of antimony. The product weighed 222·8 grains, thus showing a loss of 0·2 grain. It was harder than silver, was broken in two with a hammer, and its fracture was largely crystalline, somewhat like that of antimony, and bluish-white.

(II.) 4Ag + Sb [idem].—The quantities operated upon were 216 grains of silver and 61 grains of antimony. The product weighed 276 grains, thus showing a loss of 1·0 grain. The description of the product in the preceding experiment applies also to this, except that the colour of the fracture was greyish-white.

(III.) 6Ag + Sb [idem].—The quantities operated upon were 162 grains of silver and 30·5 grains of antimony. The product weighed 192 grains, thus showing a loss of 0·5 grain. It was hard, was broken in two with a hammer, and its fracture was granular and greyish-white.

The percentage composition of the three products in the foregoing experiments was as under:—

	I.	II.	III.
Silver	72·65	77·98	84·16
Antimony	27·35	22·02	15·84
	100·00	100·00	100·00

Specific gravity of alloys of silver and antimony.—Professor Cooke, of Harvard College, Cambridge, U.S., has determined the specific gravity of forty-eight alloys of silver and antimony; varying in richness from 50% of silver and upwards.[8] The following table contains a selection from his results: the column headed "Specific gravity calculated" shows what the specific gravity of each alloy would be, if equal to the mean of its constituents (taking the sp. gr. of silver as 10·47, and of antimony as 6·72); and the column headed "Increase in volume" shows the volume of each alloy compared with the united volumes of its uncombined constituents taken as unity:—

[6] Tr. des Ess. 2. p. 798. [7] Chemical Gazette, 1848. 6. p. 412.
[8] Communicated to the Author.

TABLE SHOWING THE SPECIFIC GRAVITY OF ALLOYS OF SILVER AND ANTIMONY.

No.	Percentage composition of alloy.		Specific gravity given by experiment.	Specific gravity calculated.	Increase in volume.
	Silver.	Antimony.			
I.	98·0	2·0	10·429	10·355	1·0072
II.	95·5	4·5	10·319	10·213	1·0104
III.	90·3	9·7	10·148	9·932	1·0216
IV.	83·5	16·5	9·933	9·587	1·0360
V.	76·2	23·8	9·777	9·241	1·0580
VI.	73·4	26·6	9·691	9·116	1·0630
VII.	70·0	30·0	9·515	8·768	1·0604
VIII.	65·0	35·0	9·243	8·759	1·0552
IX.	59·1	40·9	8·930	8·524	1·0477
X.	54·4	45·6	8·701	8·346	1·0425
XI.	50·1	49·9	8·530	8·189	1·0416

The composition of the alloys was obtained by a volumetric determination of the silver.

It will be seen that the maximum increase in volume is reached in the alloy, No. VI. of the Table, corresponding to the formula $SbAg^4$ [idem]. Cooke also found that the crystallization of the alloys became marked in proportion as the same composition is approached. He obtained small crystals approximating to the mineral dyscrasite (antimonide of silver) in the angle between the cleavage-planes.

ANTIMONIATE OF SILVER.

Before considering the joint action of air and heat on an alloy of silver and antimony, or on certain substances containing those metals in a state of chemical combination, it is necessary to inquire what is known respecting antimonial silver salts. On searching in chemical treatises and journals, I was surprised to find how little had been published on the subject. I accordingly decided to have recourse to experiment, and shall presently report the results.

All that even Berzelius states concerning antimoniate of silver is that it is white and insoluble.[9] Gmelin quotes this statement, and says not a word more.[1] H. Rose gives the following short account of its properties and mode of formation:—"A solution of nitrate of silver produces in the solution of antimoniate of potash a copious white precipitate of antimoniate of silver, which has only a slight yellowish tint. But if, on the contrary, the solution contains free alkali, the precipitate is brown, owing to the simultaneous separation of oxide of silver. Both precipitates dissolve completely in ammonia. Nitric acid throws down from the ammoniacal solution hydrated antimonic acid. If the solution [of antimoniate of potash] contains the smallest quantity of antimonious acid, the precipitate caused by the nitrate

[9] Traité de Chimie. Paris, 1831. 4. p. 422.

[1] Hand-Book of Chemistry, 1852. 6. p. 189.

of silver solution is not wholly soluble in ammonia; there then remains an insoluble black precipitate."[2] Plattner assigns the formula AgO,SbO^5 [$AgSbO^3$] to antimoniate of silver prepared in the *wet* way.[3]

The following investigation concerning antimoniate of silver was made in my laboratory, in 1870, by my friend and former assistant Mr. G. H. Hochstätter.[4] The salt was prepared by adding in excess a neutral solution of nitrate of silver to an aqueous solution of antimoniate of potash. There was thus produced a copious, white, amorphous precipitate, which contracted very much on drying, and became pale yellow when heated to redness, without changing in weight. On cooling, the pale-yellow tint almost entirely disappeared. Dilute nitric acid removed part only of the oxide of silver which it contained. By heating it with strong sulphuric acid, the oxide of silver was dissolved out and antimonic acid left. It dissolved completely in strong ammonia-water. When boiled with an aqueous solution of potash, antimoniate of potash was formed and oxide of silver separated. By digesting it for several days with sulphide of ammonium, only part of the antimony was extracted. When heated in a current of hydrochloric acid gas, it was changed into chloride of antimony, $SbCl^3$ [idem], which distilled over, and chloride of silver, which remained, aqueous vapour being also evolved.

The antimoniate of silver was analysed by the following method:—heating it in a current of hydrochloric acid gas, collecting in water the chloride of antimony evolved, precipitating the antimony in the metallic state by iron,[5] reducing the chloride of silver, left by heating it in a current of hydrogen, and weighing the silver in the metallic state. The composition of the salt, so ascertained, was as under:—

Composition per cent. of Antimoniate of Silver.

Oxide of silver, AgO [Ag^2O]	36·78
Antimonic acid, SbO^5 [Sb^2O^5]	63·11
	99·89

The composition of this salt has also been determined in my laboratory by E. Jackson, in 1875. It was prepared in the manner above described. The precipitated white antimoniate of silver, which subsided rapidly, was thoroughly washed, and then dried: on drying, it became slightly yellow. It darkened and acquired a slaty tint by occasional exposure to daylight. The method of analysis adopted was

[2] Ausführliches Handbuch d. analytischen Chemie, 1851. 1. p. 273.

[3] Die metallurgischen Röstprozesse, 1856. pp. 116, 276.

[4] My friend, who has assumed the name of Godfrey, is now, and has for several years been, at the head of the Imperial Mining Establishment of Japan. It was on his return from Cuba, where he had been engaged for several years a copper works, that he spent some time in London, and undertook the investigation in question.

[5] The method of precipitation by iron was suggested and practised with success by C. Tookey, in the analysis of alloys of antimony and tin, only the antimony being precipitated by iron.

also the same as that above described, except that the weight of the silver was calculated from that of the chloride.

COMPOSITION PER CENT. OF ANTIMONIATE OF SILVER.

Oxide of silver	36·55
Antimonic acid	64·00
	100·55

The agreement between the two analyses is not so close as might be desired, nor do the results correspond to the formula AgO,SbO^3 [$AgSbO^3$], which has been assigned to the salt in question.

The percentage composition calculated from this formula is as under:—

Oxide of silver	41·72
Antimonic acid	58·28
	100·00

Taking the mean of the two analyses, the formula $3AgO,4SbO^3$ [$Ag^6Sb^8O^{23}$] more nearly represents the composition of this arseniate of silver. Thus,

	Mean of the two analyses per cent.		Composition per cent. Calculated from the above formula.
Oxide of silver	36·58		34·94
Antimonic acid	63·42		65·06
	100·00		100·00

But I think that further investigation is required before such a formula can be accepted as correct.

COMPOUNDS AND MIXTURES CONTAINING SILVER AND ANTIMONY, HEATED IN ATMOSPHERIC AIR, ALONE AND WITH CERTAIN OTHER SUBSTANCES.

Oxide of silver and oxide of antimony heated in atmospheric air.—The following experiment on this subject is recorded by Plattner:—"Oxide of silver was mixed with an equal bulk of oxide of antimony, SbO^3 [Sb^2O^3], and the mixture was heated to redness, when it sintered a little together, and formed after cooling a dirty (*schmutzig*) dark-yellow powder; which, by further trituration in an agate mortar, acquired a bright brownish-yellow colour, and was found to be entirely free from intermixed metallic silver; some oxide of antimony was volatilized during the experiment."[8]

This experiment has been repeated in my laboratory by H. Louis (1876) with the following, somewhat different, results:—A mixture of equal bulks of oxide of silver and of oxide of antimony, SbO^3 [Sb^2O^3], was heated to low redness in a glass tube open at both ends, and slightly inclined so that a current of air kept passing through it; a little oxide of antimony was volatilized. The product consisted of

[8] Die metallurgischen Röstprozesse, p. 164.

a dull greenish-grey mass, with yellow specks, and little scales of metallic silver. Upon heating a portion of the product in a closed crucible, a button of metallic silver, containing antimony, was obtained. Another portion was heated to full redness in a muffle, whereby a dull green, apparently homogeneous mass, containing scales of metallic silver, was formed.

On analysis, 19·165 grains of this substance yielded 5·315 grains of chloride of silver, and 10·713 grains of antimony: whence it is probable that the substance had the following percentage composition :—

Oxide of silver, AgO [Ag^2O]	22·44
Antimonic acid, SbO^3 [Sb^2O^3]	75·87
	98·31

The very small quantity of metallic silver present was not determined.

Alloys of silver and antimony heated in atmospheric air.—The following experiment and analysis were made by G. H. Hochstätter in my laboratory in 1870. An alloy of silver and antimony was prepared, in which the two metals were nearly in the same ratio by weight as in the antimoniate of silver analysed by Hochstätter, namely, 42 per cent. of silver and 58 per cent. of antimony. The alloy was finely powdered and very carefully heated with free access of air. The product was brownish yellow, and with the aid of a microscope particles of metallic silver could be easily observed in it. An analysis of this substance was made in the following manner :— A portion of it was heated in a current of hydrogen, and the water thereby formed was collected and weighed. Another portion of it was acted upon by caustic potash, kept melted at the lowest possible temperature; the product was washed first with water, and then with a solution of hyposulphite of soda, in order to dissolve any oxide of silver that might be present; and, finally, the washed residue was treated with nitric acid, and the silver so separated was weighed in the state of chloride. The results of this analysis are as follow :—

	Per cent.
Oxide of silver	0·34
Metallic silver.....	37·20
Antimonious acid, SbO^4 [Sb^2O^4]	62·89
	100·43

The colour of the product would seem to indicate the presence of some oxide of silver in combination with antimonic acid. If so, the antimony could not have existed wholly as SbO^4 [Sb^2O^4].

The next experiment and analysis were made by E. Jackson in my laboratory in 1875. An alloy of silver and antimony was prepared, in which the two metals were in the same ratio by weight as in the theoretical antimoniate of silver of the formula AgO,SbO^3 [$AgSbO^3$], namely, 46·95 per cent. of silver and 53·05 per cent. of antimony. The alloy was finely powdered and calcined in a muffle

at a low temperature for about six hours. During the course of calcination the product was repeatedly weighed, until at length it ceased to increase in weight: it had a greyish-yellow tint, and with the aid of a microscope particles of metallic silver were distinctly seen in it. Its composition was found to be as under:—

	Per cent.
Metallic silver	36·70
Antimonious acid, SbO^4 [Sb^2O^4]	62·80
	99·50

The conclusion from the preceding experiments is that when an alloy of silver and antimony is heated with free access of air, no sensible quantity of antimoniate of silver is formed.

An alloy of silver and antimony, mixed with sulphate of protoxide of iron (ferrous sulphate), heated in atmospheric air. (By G. H. Hochstätter, in my laboratory, 1870.)—A mixture of 50 grains of the finely-powdered alloy, consisting of 42 per cent. of silver and 58 per cent. of antimony, and 20 grains of the *dry* sulphate of protoxide of iron, was very carefully calcined with free access of air. The product, in which with the aid of a microscope particles of metallic silver could be easily detected, was analysed nearly in the same way as that obtained by calcining the same alloy alone. Its composition was found to be as under:—

	Per cent.
Metallic silver	30·92
Sesquioxide of iron (ferric oxide)	15·23
Antimonious acid, SbO^4 [Sb^2O^4]	53·90
	100·05

Hence it appears that under these conditions sulphate of silver is not formed: but as unfortunately the temperature of calcination was not recorded, it may have been formed and subsequently decomposed. It will, however, be seen from the next experiment that probably no sulphate of silver had been formed.

An alloy of silver and antimony, mixed with iron-pyrites, heated in atmospheric air. (By E. Jackson, in my laboratory, 1875.)—A mixture of 56 grains of the finely-powdered alloy, consisting of 46·95 per cent. of silver and 53·05 per cent. of antimony, and 20 grains of iron-pyrites, was calcined in a muffle during several hours; and towards the close of the operation the temperature was accidentally allowed to get somewhat higher than was intended. The product, in which with the aid of a microscope metallic silver was plainly visible, was analysed as follows:—It was first washed with water, which dissolved out ferrous sulphate; the washed residue was heated in a current of hydrochloric acid gas, whereby chloride of antimony, $SbCl^3$ [idem], and some sesquichloride of iron, were evolved and collected in water; the residue of ferric oxide and chloride of silver was treated with hydrochloric acid, which dissolved out the former

and left practically the whole of the latter. The composition per cent. of the calcined product was thus found to be as follows:—

	Per cent.
Metallic silver	35·67
Sulphate of protoxide of iron	1·98
Sesquioxide of iron	13·15
Antimonious acid, SbO^4 [Sb^2O^4]	49·00
	99·80

Estimating the relations in weight between the iron and silver or antimony in the materials taken, and in the product, it appears that there is a notable deficiency of iron in the latter; thus showing an error in the experiment. But the results are sufficiently interesting to be recorded; especially as showing that no sulphate of silver was formed. Since the product contained sulphate of iron, it may be inferred that the temperature was not high enough to decompose sulphate of silver.

Mixed sulphides of silver and antimony heated in atmospheric air.—The following experiment, which was made in my laboratory by E. Jackson, in 1875, may be here appropriately inserted.

Sulphide of silver and sulphide of antimony were melted together in the proportions in which they occur in the mineral species pyrargyrite, namely, 68·63 per cent. of the former and 31·36 per cent. of the latter. This substance was pulverized and heated in a muffle at a low temperature; the product was yellow, and with the aid of a microscope metallic silver was perceived in it. Its composition was as follows:—

	Per cent.
Metallic silver	55·91
Sulphate of silver	18·08
Antimonious acid, SbO^4 [Sb^2O^4]	26·33
	100·32

It will be observed that the proportion of antimony compared with that of the silver is considerably less in the product than in the mixed sulphides employed: this is accounted for by the volatilization of a part of the antimony during the experiment.

The following observations upon the roasting of pyrargyrite are recorded by Plattner:—On gradually heating the mineral in a finely-divided state to incipient redness, in a clay scorifier in an open muffle, and repeatedly stirring, he found that it was changed into a pretty strongly sintered mass, which on cooling became dark brownish-grey, and contained intermixed small particles of metallic silver, for the most part in a hair-like form; sulphurous acid and oxide of antimony were evolved during the process. When a small portion of this mass, after trituration in an agate mortar, was heated to redness over an ordinary spirit-lamp in a glass tube open at both ends, there was further evolution of a little sulphurous acid and oxide of antimony; on cooling it acquired a bright brownish-grey colour, and

appeared to consist of a mixture of antimoniate of silver with a little sulphate of silver and metallic silver. On the contrary, when, during the roasting, the ore was repeatedly triturated in an iron mortar, it was finally changed after cooling from a bright brownish- to a yellowish-grey powder, which was free from metallic silver, and remained unchanged at a moderate red-heat, whilst at a higher temperature it was converted into metallic silver with the evolution of the vapour of oxide of antimony.[7]

ALLOYS OF SILVER.

Silver and Copper.

In whatever proportions silver and copper are melted together, comparatively homogeneous alloys are obtained, whether solidification takes place slowly or quickly. The colour of these alloys is white, until the copper amounts to about 50%, when it acquires a reddish tint; and beyond that proportion, it becomes more and more red as the copper increases. Silver is made more elastic and harder by the addition of copper, and, therefore, more suitable for articles exposed to friction, such as money; and as neither the beauty of its colour is sensibly impaired by the presence of a moderate quantity of copper, say about 10%, nor its capability of receiving a fine polish, nor its malleability, it is always alloyed with that metal when used for coin or plate. The hardest alloy, according to Karmarsch, consists of 5 parts by weight of silver and 11 of copper, but, according to Guettier, of 5 parts by weight of silver and 10 of copper.[8]

Dilatation by heat of an alloy of silver and copper.—Plantamour and Kirsch have ascertained that the coefficient of linear dilatation of the alloy, containing 90% of silver and 10% of copper, is 0·000018387, *i.e.* for 1° C.[9]

Fusibility of alloys of silver and copper.—According to Guettier, the alloy, which contains 10% of copper, is more fusible than silver.[1] According to W. C. Roberts, the alloy, which contains 630·29 of silver per 1000 of alloy, and which is represented by the formula $AgCu^2$ [AgCu], has a lower melting-point than silver or than any other alloy of silver and copper.[2]

Specific gravity of alloys of silver and copper.—The specific gravity of the alloys of silver and copper is less than that of the mean of the two metals. Karmarsch has ascertained the specific gravity of various alloys of silver and copper, and his results are as follow:[3]—

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[7] Die metallurgischen Röstprozesse, p. 91.

[8] Guide pratique des Alliages, 1865. p. 149.

[9] Arch. des Sci. phys. et natur., Suisse, 1870. 38. p. 37.

[1] Guide pratique des Alliages, 1865. p. 149.

[2] Proceedings of the Royal Society, 1875. 23. p. 487.

[3] Handwörterbuch der Chemie, 1859. 7. pp. 956, 957.

Weight of silver in 16 parts of alloy.	Weight of silver per cent.	Specific gravity of the alloy.
3	18·75	9·127
4	25·00	9·231
5	31·25	9·335
6	37·50	9·439
7	43·75	9·544
8	50·00	9·648
9	56·25	9·752
10	62·50	9·856
11	68·75	9.961
12	75·00	10·065
13	81·25	10·169
14	87·50	10·273
15	93·75	10·377

Wertheim has found the sp. gr. of the alloy containing 90% of silver and 10% of copper, *i.e.* corresponding to the formula Ag^6Cu^2 [Ag^6Cu], to be 10·121, and of the alloy containing 61·72% of silver and 38·28% of copper, *i.e.* approximating to the formula $AgCu^2$ [AgCu], to be 9·603.[4]

Note on the mode of calculating the specific gravity of alloys.—As an erroneous method of calculating the specific gravity of an alloy from the specific gravities and weights of its component metals, on the assumption that its volume is equal to the sum of the volumes of its component metals, has not unfrequently been adopted, the following note on the subject may be useful.[5]

Let S and C be the weights of the silver and copper in an alloy of those two metals, and s and c their respective specific gravities. Then $\frac{S}{s}$ and $\frac{C}{c}$ will be their respective volumes, say V and V^1.

And let σ be the specific gravity of the compound. Then, since the weight of the compound equals the sum of the weights of the constituents, we have—

$$(V + V^1)\,\sigma = VS + V^1C;$$
$$\therefore \sigma = \frac{VS + V^1C}{V + V^1}.$$

Imperfect homogeneity in alloys of silver and copper.—It has been stated that the products of the fusion of silver and copper in any proportions are *comparatively* homogeneous. Yet it has long ago been remarked that ingots of alloys of these metals are not absolutely indentical in composition throughout, and that, in some cases, the central portion is poorer in silver than the exterior. Thus Cramer asserted that "when silver is alloyed with copper, and cast into bars [*i.e.* into open ingot-moulds of the usual form, trapezoidal in cross-section], it is observed that the bottom is richer in silver by a few grains than the top. The thicker the bars and the slower the solidification of the metal, the greater is the difference. In the

[4] Ann. de Chim. et de Phys. 1844. 12. p. 595.

[5] See Goodwin's Elementary Course of Mathematics. Cambridge, 1857. p. 434.

case of metal left to cool in large crucibles in the furnace, even if the mean of the returns on the portions cut out from the top and the bottom be taken, this is not correct. A nearer approximation may be obtained by rejecting the half of the difference between the upper and lower returns: *e.g.*, suppose the upper portion to contain 3 oz. 10 grs. in the mark, and the lower 3 oz. 14 grs.; the upper is to be taken as 3 oz. 12 grs., and the mean return on the whole 3 oz. 11 grs.: this has been taught by experience. But there is no surer method than to granulate a dip-assay [*i.e.* a portion taken by a ladle from a mass of metal while molten], and to assay the granules, if circumstances allow it, and if the pieces to be assayed are of great importance and hence worth the trouble."[6]

Jars published the following observations on this subject:—"I have found by experiments that in order to render ingots of '*billon*' [*i.e.* an alloy containing 80% of copper and 20% of silver] more uniform in composition throughout, it was necessary that the ingot-moulds should be as hot as possible; and that the less they were heated the greater was the inequality. That led me to make many special assays, and I ascertained from experiments made at official assay-offices, as well as from my own, that in cases where the difference was greatest, it was the centre of the ingot which was poorest in silver; and all the external parts the richest, especially those which had touched the sides of the ingot-mould. M. Cramer mentions this inequality in his treatise on assaying; but he had perhaps not thought that it might be also sensible in the case of alloys of silver and copper, without admixture of any other metal."[7] Jars, however, was mistaken in this opinion; as is shown by the extract from Cramer's treatise immediately preceding.

This question, which is very important in relation to silver coinage, was investigated at the Mint in Paris, in the years 1824 and 1825, by D'Arcet, Inspector-General of Assays. A series of ingots was prepared in which the proportion of silver per 1000 ranged from 100 to 950 inclusive, and increased by tenths from one extreme to the other; and it was found that in those which contained from 50 to 300 parts of copper per 1000 of alloy, the central part was richer in silver than the external, while in those which contained from 300 to 900 parts of copper per 1000 of alloy, the reverse was the case. The ingots were mostly cast in open moulds. Numerous attempts were made to produce ingots identical in composition throughout, but in vain; and the hope of solving that important problem was abandoned.[8]

Levol has prosecuted the inquiry, and arrived at interesting results. He cast the metal sometimes in the form of a cube, but oftener in that of a sphere, using closed moulds of cast-iron for that purpose. The height of the cube was 42 millimetres (about $1\frac{2}{3}$in.):

[6] Anfangsgründe der Metallurgie. Blankenburg und Quedlinburg, 1775. 2nd part, p. 15.

[7] Voyages métallurgiques, 1781. 3. p. 269.

[8] Mémoire sur les Alliages, considérés sous le Rapport de leur Composition chimique. Par M. A. Levol. Ann. de Chim. et de Phys. 1852. 3. ser. 36. pp. 193 et seq.

the feeders or "gets" were about 50 mm. (about 2 in.) high, 8 mm. (about $\frac{5}{16}$ in.) wide at the bottom, and 17 mm. (about $\frac{11}{16}$ in.) at the top. The sphere was 50 millimetres (about 2 in.) in diameter: the feeders were about 50 mm. (about 2 in.) high, 12 mm. (about $\frac{1}{2}$ in.) wide at the bottom, and 21 mm. (about $\frac{13}{16}$ in.) at the top. The ingot-moulds, after pouring the metal, were probably left to cool in the air: but there is no special statement upon that point. The weight of the ingots, exclusive of the feeders, was from 600 to 700 grammes (from 1·32 to 1·54 lb. avoirdupois). Portions from the external surface, and different parts of the plane obtained by sawing the ingots in two through the axis of the feeders, were analysed; and in every case an analysis was made of a sample of the alloy, prepared by stirring it when melted, and granulating a little of it in water immediately afterwards. The alloys operated upon by Levol were made according to the following formulæ:—

No.	Formula of alloy.	Form of ingot.	Silver, per 1000 parts by weight of alloy. Calculated.	Found in the granulated sample.
I.	$Ag + Cu\ [Ag^2 + Cu]$	(*a*) Cubical	773·3	773·15
		(*b*) Spherical ...	773·3	774·175
II.	$Ag + Cu^2\ [Ag + Cu]$	Spherical	630·35	631·925
III.	$Ag^2 + Cu^3\ [Ag^4 + Cu^3]$	Spherical	694·50	693·70
IV.	$Ag^3 + Cu^5\ [Ag^6 + Cu^5]$	Spherical	671·73	672·9
V.	$Ag^3 + Cu^4\ [Ag^3 + Cu^2]$	Spherical	718·93	718·32
VI.	$Ag^2 + Cu\ [Ag^4 + Cu]$	Spherical	872·0	873·0
VII.	French standard silver	Spherical	900·0	901·34
VIII.	Alloy richer than standard	(*a*) Cubical	950·0	947·0[a]
		(*b*) Remelted and cast spherical	950·0	948·39

I. (*a*) and (*b*). The ingots were far from homogeneous, the proportion of silver progressively increasing from the exterior to the centre. The results with the spherical ingot were more concordant than those with the cubical, as to the composition of the metal in points symmetrically disposed in both [except with the alloys containing 900 and 950 parts by weight of silver per 1000]. In the cubical ingot the extremes in the proportion of silver were 783·18 in the centre, and 770·15 at the middle of the upper edge of one side. The mean proportion in the external parts was 772·95.

II. The ingot was very far from homogeneous, the proportion of silver increasing rapidly from the centre to the exterior. The extremes were 619·0 of silver in the centre, and 634·0 at the top in contact with the bottom of the feeder. The mean proportion of silver in the external parts was 633·31.

III. The mean proportion of silver in three pieces from the centre was 693·71—the extremes being 693·4, and 694·1; and in six from the exterior was 693·84,[1]—the extremes being 693·65 and 694·0. The

[a] Levol considers that there must have been an error in weighing out the metals in this case.

[1] The number given by Levol is 693·34; but it is evidently a typographical error, and should be as stated in the text.

ingot was re-melted and again cast in the spherical form. The granulated sample contained 694·1 of silver per 1000. The mean proportion of silver in two pieces from the centre was 693·775, and in six from the exterior was 694·33. But in this case were analysed two portions taken from above and two portions from below the centre,—the mean proportion of silver in the former was 690·35, and in the latter 696·55, while the composition of the centre was nearly the same as that of the granulated sample and in the external parts: it seems, as Levol remarks, that there was a tendency in the two metals to separate during cooling, and range themselves according to their specific gravity. This is the only result of the kind observed by Levol during his investigation, and he considers that it explains why this alloy easily yields crystals: by slowly cooling about 1 kilogramme of the melted alloy he obtained octahedra, of which the sides were several millimetres in length.

IV. The mean proportion of silver in two pieces from the centre was 671·8, and in the external parts 673·75.

V. The proportion of silver in a piece from the centre was 718·13, and the extremes, in six portions from the exterior and eight from the interior, taken excentrically, were 717·7 and 718·32. The top of the feeder contained 717·88, and the bottom 718·06 of silver. The ingot may, therefore, be regarded as practically identical in composition in every part. Levol ascertained that when this alloy was cast in open moulds the ingots were equally homogeneous throughout. The calculated specific gravity of this alloy is 9·998; but Levol found that the specific gravity of a piece from one ingot was 9·897, and that of a piece from another was 9·912; the mean = 9·9045. Admitting the accuracy of Levol's results, the conclusion is, that when the proportion of silver exceeds that in this alloy, there is a tendency towards the concentration of silver in the centre, and, when the contrary is the case, there is an opposite tendency.

VI. The proportion of silver in the centre was 881·78, and the mean proportion in the external parts 872·5.

VII. The proportion of silver in the centre was 907·31, and the mean proportion in six pieces from the exterior 898·95,—the extremes being 898·43 and 900·0. The same ingot was re-melted and cast cubical; the granulated sample contained 903·13 of silver per 1000. The proportions of silver were as follow:—in the centre, 909·5; mean of six of the angles, 900·06; mean of pieces from three edges, 900·14; mean of pieces from four sides, 900·33. The proportion of silver in the granulated sample exceeds that in the external parts by 2·675 per 1000; and that in the centre exceeds the average in the external parts by 8·83. Hence marked liquation occurs during the solidification of this alloy, and hitherto no means of preventing that result has been discovered.

VIII. (*a*) The proportion of silver in the centre was 950·0, and the mean proportion in the external parts 947·09. (*b*) The proportion of silver in the centre was 950·0, and the mean proportion in the external parts 947·7.

Levol determined the composition of different parts of a bar or ingot of the alloy made by melting together 900 parts by weight of silver and 100 of copper; the ingot was 50 centimetres long (1 ft. 7·69 in.), and when rolled out into a strip, or, as it is termed, a fillet, was 1·70 metre long (5 ft. 6·9 in.). Such a fillet yields 40 blanks of 5-franc pieces, and the proportion of silver in each of these was ascertained from the top of the rolled-out ingot to the bottom. The extremes were 900·44 of silver per 1000 in the blank from the top, and 897·3 in that from the bottom. The mean proportion of silver in the 40 blanks was 898·8965.

It occurred to Levol that, in melting silver and copper together with access of air, oxygen might be absorbed and affect the homogeneity of the ingots; and from the following single experiment he inferred that such is the case. About 6 kilogrammes of the metalliferous residues (*lavures*, i.e. the metal obtained by pounding various matters, such as crucibles, bricks, etc., impregnated more or less with metal, and washing so as to separate the lighter, so-called earthy, and other foreign matters) from a cast of what was then the only French standard silver (*i.e.* containing 100 parts of copper per 1000 of alloy) were melted with nitre, in order to separate iron, which was present in considerable quantity; and after well stirring the molten metal, samples of it were prepared by granulation, after which it was poured into an ingot-mould. The assays of the samples varied from 6 to 7 thousandths from the poorest to the richest; and variations equally great were found in different and corresponding parts of the ingot. The fracture of this ingot is stated to have been peculiar; on a dull white ground, proper to an ingot of this composition, were irregularly distributed numerous red stains of dioxide of copper, producing an appearance suggestive of the cut surface of marbled soap. The ingot was re-melted and stirred repeatedly, yet without causing any change in that respect. Levol tried to reduce the oxide, which he supposed to exist in this alloy, by means of iron, but without the least success. He then tried the effect of charcoal upon the surface of the molten metal, and with a better result; but the operation was very long, owing to the small extent of metallic surface in contact with the charcoal. He records the fact that during 40 years prior to 1764, it was the practice at Lyons to melt "the oxidized alloy of silver and copper" in a round crucible, at the bottom of which pieces of charcoal were kept depressed; effervescence occurred, and the workmen said that in this manner they "*work*" the silver; and accordingly, Levol recommends its adoption in similar cases. He also suggests that "probably this method might be equally useful for copper, and that it would deserve a trial in order to verify the fact." From this, it would seem that Levol had no practical knowledge of the process of *poling* copper.

My friend and former student Mr. W. C. Roberts, Chemist to the Royal Mint, has recently conducted an elaborate series of experiments upon alloys of silver and copper, with special reference to their

homogeneity.[2] He cast the alloys in cubical moulds of firebrick, about 45 mm. to the side (internal measurement), in which they could be cooled either comparatively rapidly, or slowly and uniformly. When it was desired to cool the metal slowly, the mould was placed in a crucible and heated in a melting-furnace to a higher temperature than the melting-point of silver; it was then withdrawn, the metal poured in, the mould and crucible replaced in the furnace, and the fire allowed to die out; so that the metal remained liquid for an hour or two. When the metal was to be cooled quickly, the mould was only warmed sufficiently to prevent the risk of fracture; and solidification took place almost as soon as the mould was filled.[3] The following table contains a summary of Roberts' results:—

TABLE SHOWING THE RESULTS OF ROBERTS' EXPERIMENTS ON THE HOMOGENEITY OF ALLOYS OF SILVER AND COPPER, AND THE EFFECT OF SLOW COOLING.

No.	Designation of alloy.	Parts of silver contained in 1000 of alloy.	Rate of cooling.	Maximum variation in the quantity of silver in different parts of the alloy.
I*a*.	British standard coin...	925·0	rapid	12·8 per thousand.
I*b*.			slow	1·4 „
II*a*.	Older French standard coin.....	900·0	rapid	10·1 „
II*b*.			slow	1·3 „
III.	Levol's homogeneous alloy	718·93	slow	1·2 „
IV.	$AgCu^2$ [AgCu].....	630·3	slow	21·1 „
V.	$AgCu^5$ [$AgCu^4$]	333·3	slow	12·8 „

In I*a*. and II*a*., the centre of the cubes was the richest portion, and the corners were the poorest.

In I*b*. and II*b*., the slight variations in richness appear to have followed the same law.

In III., the corners were generally richer than the centre.

In IV., Roberts suggests that "the action of gravity appears to have influenced the arrangement, the lower parts of the cube being richer than the upper."

In V., the variations in richness do not appear to have followed any law.

It will be seen that the effect of slow cooling upon the alloys containing 900 and 925 of silver is to render them almost homogeneous; and this is perhaps the most important result which Roberts obtained.

Col. Smith has been led to the conclusion, from a long series of experiments made for Indian mints, "that the separation of the constituent parts of an alloy containing $91\frac{2}{3}$ per cent. of silver [and the rest copper] was not so much due to the rapidity or slowness with which the heat of the fluid metal was abstracted, as to the inequality

[2] Proc. Roy. Soc. 1875. 23. p. 481.
[3] These details were personally communicated to the Author.

affecting its removal from different parts of the melted mass in the act of solidification." He found that coinage-ingots, about 15 in. high, $2\frac{1}{2}$ in. broad, and $\frac{5}{8}$ in. thick, which were cast in vertical iron moulds, "were *uniformly* finer [*i.e.* richer in silver] at their upper surface and coarser at their sides and bottom, especially at the corners." This, however, was prevented and the reverse effect produced by cooling the ingots from their upper surface only. "After many experiments, it was satisfactorily established that, whatever form the metal might take, the act of cooling caused a partial separation of the copper towards the surfaces from which the heat was abstracted, those parts of a bar or ingot being finest which congealed the last."[4]

Effect of roasting alloys of silver and copper.—When a pretty strongly cupriferous alloy of silver is roasted with access of air, both metals are oxidized, but the copper in much larger proportion than the silver; and the same result occurs on fusion with nitre.[5]

When alloys of silver and copper are heated in a muffle, superficial oxidation and consequent discoloration occur, and by this means some indication may be obtained as to the proportion of copper in certain of these alloys. The alloy should first be rolled or flattened out under the hammer, and then *very slightly* heated to redness in a muffle, as a high temperature would give different results. For the following table we are indebted to Chaudet:[6]—

Silver in 1000 parts of alloy.	Characters of the surface after heating.
1000 (*i.e.* pure silver)	Dull but white.
950	Uniform grey-white.
900	Dull grey-white, black fillet at the edges.
880	Grey, almost black.
860	Grey, almost black.
840	Quite black.
820	Quite black.
800	Quite black.

Hence it appears that this method of approximately estimating the proportion of copper ceases to be applicable in the case of alloys containing 160 parts or more of that metal, per 1000 of the alloy.

Action of sulphur on alloys of silver and copper.—When an alloy of silver and copper is heated sufficiently with sulphur, both metals are sulphurized, but the copper in greater proportion than the silver. Thus, I heated to bright redness in a clay crucible an ingot of such an alloy, which contained 26% of silver and weighed 36 lbs. 15 ozs. avoirdupois, and added sulphur in successive portions, stirring well, and raising the temperature at last, so as to render the contents of the crucible very liquid: the product was poured into a flat, closed ingot-mould of cast-iron, and consisted of regulus much resembling disulphide of copper, and white metal, which contained 57% of silver

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[4] Proc. Roy. Soc. 1875. 23. p. 433.
[5] Berthier, Tr. des Ess. 2. p. 796.
[6] L'Art de l'Essayeur. Par M. Chaudet, ex-Essayeur des Monnaies de France. Paris, 1835. pp. 77, 78.

and weighed 9 lbs. 6 ozs. avoirdupois. The metallic portion subsided well, and was readily detached from the regulus. The temperature found to be most suitable for sulphurization was that at which the alloy and regulus were somewhat pasty. By stirring, while in this state, it was easy to bring the metal and sulphur in contact; but, if the temperature sufficed to render the metal and regulus formed very liquid, it was difficult to effect combination between the former and the sulphur added. By repeated additions of sulphur under the conditions stated, the whole of the alloy was converted into regulus. There is of course much waste of sulphur in such a process, and in one experiment the cost amounted to $3\frac{1}{2}d.$ per lb. of alloy sulphurized. The items are as under:—

Weight of ingots treated	105 lbs.
Regulus obtained	93¾ „
Metal left unsulphurized	30 „

1 or 2 lbs. of iron were dissolved from the rod used in stirring.

	£	s.	d.
3 sacks of coke at 2/6	0	7	6
Man, 1¼ day at 5/6	0	6	10½
Boy, 1½ day at 1/6	0	2	3
2 casting-pots at 1/-	0	2	0
Sulphur, 56 lbs. at 7/- per cwt.	0	3	6
	£1	2	1½

In 1800 Napioné, in Paris, suggested the application of the foregoing fact to the treatment of argentiferous alloys of copper, which contained, say from $\frac{1}{12}$ to $\frac{1}{4}$ of silver, such as the monetary alloys then current and designated "billon." He experimented on the subject on the large as well as the small scale, seemingly with much care, and published a detailed account of his results.[7] He melted in a crucible 22 ozs. (1 oz. = 0·9837 oz. troy) of argentiferous copper, containing about 29% of silver, added thereto 2 oz. of sulphur, and poured the molten product into a conical ingot-mould: this product consisted of regulus and metal in two layers, which when cold were easily detached from each other by a blow with a hammer. The metal left unsulphurized was subjected twice to that process; and after the three operations the total regulus and metal weighed respectively, 21 ozs. 22 deniers (1 oz. = 24 deniers = 576 grains), and 4 ozs. 16 deniers 12 grains. The metal contained about 75% of silver: was tolerably malleable, yet, owing to the presence of a little sulphur, cracked at the edges when hammered out flat. The regulus contained about 11% of silver, or 7 deniers 16 grains per mark. Experiments were made upon the argentiferous regulus with a view to its desilverization by amalgamation; and the original record of them may still be read with advantage.

On the large scale a quintal (100 lbs.) of "billon" was melted in

[7] Exposition d'une nouvelle Méthode pour séparer l'Argent qui se trouve allié au Cuivre dans la Monnaie de billon; par le C^en. Napioné. Journ. des Mines, 9. No. 58, p. 791.

a brasqued copper-refining hearth, and sulphurized by the addition of sulphur. After the removal of the charcoal used as fuel, one man projected the sulphur from a long-handled iron ladle upon the molten metal, while another stirred the latter with a rod of clay. As soon as sufficient regulus had formed, the surface of the bath was sprinkled over with water by means of a wet broom, and the regulus thus solidified was removed with an iron fork. By repeating this operation several times as quickly as possible, regulus and metal were obtained in nearly the same proportions as in the small experiments. In another trial 1½ quintal was sulphurized with equal success.

Japanese Alloys of Silver and Copper.—According to Pumpelly, who obtained his information direct from native workmen, the Japanese use alloys of silver and copper, in which the proportion of silver ranges from 30 to 50 per cent. Articles made of such alloys acquire a rich grey colour by boiling them, after polishing, in a solution of sulphate of copper, alum, and verdigris. These alloys are used for sword ornaments, pipes, and a great variety of objects; and the grey colour, produced in the manner described, is much liked by the Japanese. The solder used for these alloys consists of 10 parts by weight of silver, 5 of brass (composed of 10 of copper and 5 of zinc), and 3 of zinc. This solder is also used for silver; but for the substance named "Mokume," the solder consists of 10 of silver and 1½ of the same kind of brass as that above mentioned. According to Pumpelly, the name "Mokume" is applied to "several alloys and metals of different colours associated in such a manner as to produce an ornamental effect. Beautiful damask work is produced by soldering together, one over the other in alternate order, thirty or forty sheets of gold *shakdo* (alloy of copper and gold containing from 1 to 10 per cent. of gold), silver, rose-copper, and *gin shi bu ichi* (alloy of silver and copper), and then cutting deep into the thick plate thus formed with conical reamers, to produce concentric circles, and making troughs of triangular section to produce parallel, straight or contorted lines. The plate is then hammered out till the holes disappear, manufactured into the desired shape, scoured with ashes, polished, and boiled in the solution already mentioned." It should be added that the alloys of copper and gold acquire a beautiful bluish-black colour when, after polishing, they are boiled in the solution above mentioned. "The intensity of the colour, and, to a certain extent, the colour itself, are proportionate to the amount of gold, 1 or 2 per cent. producing only a rich bronze colour. Pure copper treated in the above solution received the appearance of an enamelled surface with a rich reddish tint, and brass a similar surface with a darker shade." In the case of the gold and copper alloys, Pumpelly supposes that the superficial removal of the copper by the solution exposes a thin film of gold, and that the blue colour produced is in some manner due to the action of light on this film.[8] An

[8] Notes on Japanese Alloys, by Raphael Pumpelly, American Journal of Science and Arts, v. 42, July 1866.

extensive series of these and other Japanese alloys has been presented by Mr. G. H. Godfrey to the Museum of Practical Geology in Jermyn Street, where they are exhibited.

Silver in ancient Roman Bronze and Copper Coins.—J. A. Phillips has found silver in notable quantity in several ancient Roman coins. Out of ten analyses of such coins which he has recorded the two following show the largest proportions of silver:—

	Sp. gr.	Copper.	Tin.	Lead.	Iron.	Zinc.	Silver.
I.	8·71	— 84·70 ..	3·01 ..	2·67 ..	0·31 ..	trace ..	7·93 = 98·62
II.	8·70	— 91·46 ..	— ..	— ..	2·31 ..	— ..	5·92 = 99·69

Dates and descriptions of these coins:—I. Claudius gothicus. A.D. 268. Inscription on the obverse, "Spes publica." II. Tacitus. A.D. 275. Inscription on the obverse, "Pax publica."[9]

SILVER COIN AND PLATE.[1]

British silver coin and plate.—The proportion of silver in coin and plate is regulated by law, as is also the proportion of gold in gold coin and plate. It is enacted that British silver coin shall consist of 11 ozs. 2 dwts. of fine silver and 18 dwts. of copper in the troy pound. This is termed sterling silver. In expressing the proportion of silver the word standard is commonly used: thus, sterling silver is said to be of the standard of 11 ozs. 2 dwts., the unit of weight being always the pound troy of 12 ozs. or 240 dwts. It is the exact equivalent of the French "titre," with the exception that in France the unit of weight is 1000 grammes or 1 kilogramme. British coin in France would be designated as of the "titre" or standard of 925, *i.e.* in 1000 parts by weight there are 925 of silver. The word *alloy*, or as it was formerly written allay, is technically restricted to the copper with which the silver is combined; and this is also the case with alloys of gold and copper. A chemist would say that standard silver is an *alloy of silver and copper*, and an assayer or bullion-dealer that it is *silver containing* 18 dwts. *of alloy* (in the pound troy), *i.e.* 7·5% of copper. It is important to bear in mind this double meaning of the word. The term base metal is used as synonymous with alloy in the last-named sense. Thus standard silver is said to consist of 37 parts fine metal, and 3 parts base. According to Johnson, alloy or allay "is derived by some from *à la loi*, according to law; the quantity of metals being mixed according to law: by others, from *allier*, to unite; perhaps from *allocare*, to put together."[2] With regard to the word *sterling*, the same authority states, that of the many derivations

[9] Quart. Journ. of the Chem. Soc., 4. p. 252. Jahresber. 1851. p. 685.

[1] "By the word silver we understand, not only the metal so called, pure and unmixed, but also when in a mass with copper; and if but one-half, two-thirds, or any other proportional part of it be silver, yet the whole bears that name." The Doctrine of Gold and Silver Computations, by Thomas Snelling. London, 1766. p. 1.

[2] Dictionary of the English Language, 1805.

which have been offered, the most probable is that proposed by Camden, who thus writes: "They are much mistaken who think that our good and lawful money of England, commonly called *sterling* money, takes its name from hence (*i.e.* Stirling Borough and Castle); for that came from the Germans, who were termed Easterlings by the English, from their living Eastward; and who were first called in by King John to reduce the silver to its due fineness; and such money in ancient writings is always called *Easterlings*."[3] In a well-known old book it is stated that the expression *sterling allay* is derived "from the *Easterlings*, or men that came from the *East* part of Germany in the time of King *Richard* the First, and who were the first contrivers and makers of that allay."[4] Wedgwood maintains that how or when the word originated is unknown. (Dict. of Engl. Etymol. 1872.)

According to Ryland, the first statute made for regulating the standard of gold and silver, to be used by the workers in these metals in England, is that of the 28th Ed. I. c. 20 (A.D. 1300). It ordains that goldsmiths shall make "No worse gold than of the touch [*i.e.* synonymous with sign or mark] of Paris," and "silver of the sterling allay, or of better, at the pleasure of him to whom the work belongeth; and that none work worse silver than money."* This standard was 11 ozs. 2 dwts., and was first particularly defined by statute in 1576, by the 18th of Elizabeth, c. 15. It continued unchanged from the time of the Conquest down to that period, except from the 34th of Henry VIII. (A.D. 1542) to the 6th of Edward VI. (A.D. 1552), during which interval it was altered several times.[5] In 1696 the standard was raised to 11 ozs. 10 dwts. by the 8th of William III. c. 8, in order to prevent the conversion of coin into plate. By the 6th of George I. c. 2, ss. 1 and 41, the old standard of 11 ozs. 2 dwts. was revived concurrently with that of 11 ozs. 10 dwts.; and these two standards still exist, though only the former is in use. Mr. Ryland says "the reason assigned in the preamble is, that manufactures of silver which were made according to the old standard

[3] Quoted from an excellent and useful work by my friend Mr. Arthur Ryland, of Birmingham, entitled "The Assay of Gold and Silver Wares; an Account of the Laws relating to the Standards and Marks, and of the existing Assay Offices." London, 1852. p. 2.

[4] "A new Touch-Stone for Gold and Silver Wares," 2nd ed. London, 1679. p. 8. It is a book full of historical and other information of interest.

* Idem, p. 10.

[5] The following are the changes stated by Mr. Ryland:—

		Standard oz.	dwt.
1542.	34 Henry VIII.	10	0
1544.	36 ,,	6	0
1545.	37 ,,	4	0
1547.	1 Edw. VI.	4	0
1549.	3 ,,	6	0
1550.	4 ,,	6	0
1551.	5 ,,	3	0
1552.	6 ,,	11	1
1553.	1 Mary	11	0

This last statement respecting the change of standard does not agree with that previously made,—which is correct,—to the effect that the old standard continued unchanged, except from the 34th of Henry VIII. to the 6th of Edward VI.

of 11 ozs. 2 dwts. of fine silver were more serviceable and durable than those made of the standard of 11 ozs. 10 dwts."[6]

At the present time (1877) only five denominations of silver coins are struck at the Mint in London, namely, the half-crown, florin, shilling, sixpence, and threepenny piece. The dimensions of the ingots or bars used for each denomination of coin, and the diameter and weight of each coin, are shown in the following table :—

DIMENSIONS OF SILVER BARS.

	Length.	Breadth.	Thickness.
	Inches.	Inches.	Inches.
Half-crown	26	$2\frac{2}{16}$	$\frac{3}{8}$
Florin	26	$2\frac{1}{16}$	$\frac{3}{8}$
Shilling	22	2	$\frac{3}{8}$
Sixpence	22	$1\frac{1}{8}$	1
Threepence	22	1	1

DIAMETER AND WEIGHT OF THE COINS.[7]

	Diameter.	Weight in troy grains.	Weight in decimal fractions of troy ounce.
	Inches.		
Half-crown	1·2720	218·1818	0·4545
Florin	1·1826	174·5454	0·3636
Shilling	0·9296	87·2727	0·1818
Srxpence	0·7648	43·6363	0·0909
Threepence	0·6383	21·8181	0·04545

The law requires that the quality of the metal of all silver wares, with certain exceptions, shall be determined by assay at offices in various parts of the kingdom duly authorized for that purpose; and that if it be found equal to standard, it shall be stamped at those offices with a series of marks, which indicate the maker, the quality of the standard, the place of assay, the year of assay, and the payment of duty. The name of the maker is indicated by his initials,—the standard of 11 ozs. 2 dwts. by a Lion Passant, and that of 11 ozs. 10 dwts. by a Lion's Head erased (*i.e.* without the body), except at Birmingham and Sheffield, and there by Britannia alone,—the place of assay by heraldic arms,—the year of assay by a letter, which is used throughout the year and is changed every year,—and the payment of duty by the Sovereign's Head. There are seven Assay Offices in England, for which the Arms are as follow :—London, a Leopard's Head, the Arms of the Goldsmiths' Company,—Birmingham, an Anchor,—Chester, a Sword between three Garbs,—Exeter, a Castle with three Towers,—Sheffield, a Crown,—Newcastle-upon-Tyne, Three Castles, with the addition of the Leopard's Head,—and York, a Cross and five Lions, also with the addition of the Leopard's Head.[8] There are two Assay Offices in Scotland, one in Edinburgh and the other in Glasgow, where a series of marks corresponding with the English is used; but the standard is indicated by the Thistle, with the addition of Britannia in the case of the standard of 11 ozs. 10 dwts. Ryland states that the peculiar marks are "Edinburgh, a Castle; Glasgow, a tree growing out of a mount

[6] Op. cit. p 32.
[7] A Treatise on Coining, by George F. Ansell, of the Royal Mint, 1862. p. 26.
[8] Ryland, p. 36.

with a bell pendent on the sinister branch, and a bird on the top branch, over the trunk of a tree a salmon in fesse, in its mouth an annulet. The office at Glasgow has not adopted the marks prescribed by this statute, but has continued those previously in use by them; the only difference, however, is that the lion rampant takes the place of the thistle."[1]

In Ireland the assaying and marking of wrought gold and silver plate is restricted to the Goldsmiths' Company in Dublin. A series of marks, corresponding to the English, is also used. The standard, which is 11 ozs. 2 dwts., and the place of assay, are indicated by a Harp Crowned,—and the payment of duty by the figure of Hibernia, with an additional mark of the Sovereign's Head, according to an enactment of 47th George III., without any reference to that of Hibernia, which had been prescribed for the same purpose by the Commissioners of Excise in 1730.[1]

By the 55th George III. c. 185, all manufactured silver articles, with the exception of such as are not required to be assayed, are chargeable with a duty of 1*s.* 6*d.* per ounce, calculated on five-sixths of the weight of the article when assayed, one-sixth being allowed for waste in finishing. The exceptions are (30th George III. c. 31, ss. 3 & 4), without reference to weight,—chains,—necklace beads,—lockets,—filigree work,—shirt buckles or brooches,—stamped medals,—spouts to teapots of china, stone, or earthenware: with reference to weight,—tippings, swages, or mounts not weighing 10 dwts. of silver each, except necks and collars for castors, cruets, or glasses, appertaining to any sort of stands or frames: and all articles not weighing 5 dwts. each, except necks, collars, and tops for castors, cruets or glasses, appertaining to any sort of stands or frames,—buttons for wearing apparel,—solid sleeve buttons,—solid studs not having a bishilled edge soldered on,—wrought seals,—blank seals,—bottle tickets, — shoe-clasps, — patch-boxes, — salt-spoons, — salt-shovels, — salt-ladles, — tea-spoons, — tea-strainers, — caddy-ladles, — buckles, short buckles or brooches excepted,—pieces to garnish cabinets or knife-cases, or tea-chests, or bridles, or stands, or frames.[2]

French silver coin and plate.—The alloys of silver and copper until recently legal in France were as under:[3]—

	Specific gravity.	Copper in 1000 parts.	Errors tolerated. Copper in 1000 parts.
Silver coin	10·257 to 10.306	100	103 to 97
Coin, named "billon" ..	9·326 to 9·508	800	807 to 797
Silver plate	..	50	55 to 50
Silver medals	..	50	53 to 47
Silver jewelry	..	200	..
Silver solder	..	120 to 330	..

[1] Ryland, op cit. p. 110. For information on such points the reader may consult the valuable book of Mr. W. Chaffers, entitled "Hall Marks on Gold and Silver Plate," with Tables of annual Date Letters employed in the principal assay offices of England, Scotland, and Ireland, from the earliest period of their use to the present day; with extracts from the statutes and ordinances regulating the manufacture and stamping of the precious metals. To which are added Fac-similes of the Stamps on Standard Plate of English and Foreign Manufacture. 3rd ed. 1868.

[1] Idem, p. 123.

[2] Idem, p. 159.

[3] Chaudet, L'Art de l'Essayeur, 1835. pp. 355 et. seq. Complete information

The coins consisting of "billon" were pieces of ten centimes, but none have been made since 1810.

The standard for all French silver coins under the five-franc piece has been lowered to 835 of silver per 1000 of alloy.

Oxide of copper in silver coin.—According to Riemsdijk, oxygen is a general, if not universal, constituent of silver coin. He heated various coins in a current of hydrogen, and found as little as 0·006% to 0·009% of oxygen in Belgian 5-franc pieces, and as much as 0·068% in a Dutch half-florin. He supposes that the oxide of copper formed in the process of annealing the metal from which the coins are made is only partially removed by the *pickling-liquor* (*i.e.* the water, acidulated with from about 3·0% to 5·0% of mono-hydrated sulphuric acid, used for whitening the surface of the metal). More oxygen is retained when the metal is thrown red-hot into the pickling-liquor than when it is previously allowed to cool and subsequently boiled in it: this he supposes to be due to the superficial layer of silver being more compact, and the oxide of copper therefore less easily attacked by the acid, in the former case than in the latter.

Riemsdijk had made most of his experiments before he became aware of Graham's researches on the occlusion of gases by metals (see p. 17, *antea*); the light thus thrown upon his own investigation led him to conclude that a part of the oxygen "is fixed, without any doubt, in a physical manner by the silver of the alloy." The supposition, that the whole of the oxygen may be occluded, appears to be negatived by the fact, noticed by Riemsdijk, that, the stronger the pickling-liquor, the smaller the proportion of oxygen retained by the metal.[4]

Lead in silver coin.—Eliot and Storer have detected the presence of a sensible quantity of lead in silver coins from the United States' Mint and from other sources.[5] Their results are as follow:—

Kind of coin.	Standard (*i.e.* silver per 1000 of alloy).	Lead per cent.
1 American half-dollar of 1824	900	0·3100
20 American 5-cent pieces of 1853	900	0·2090
10 American 5-cent pieces of 1854	900	0·2282
2 American 25-cent pieces of 1858	900	0·2305
Fine silver from U. S. Assay Office in New York, 1860	..	0·1611
1 Spanish dollar of 1793, Carolus IV.	..	0·0558
1 Mexican dollar of 1829	..	0·0434
2 English shillings of 1816	925	0·4847
1 French 5-franc piece of 1852, Napoleon III.	900	0·4282

concerning the coins of the world will be found in one of the most useful books published, entitled "J. C. Nelkenbrecher's Allgemeines Taschenbuch." Berlin. New editions are brought out from time to time. The 18th edition is dated 1858. This book also contains a complete account of weights and measures, old as well as new.

[4] Mémoire sur la Composition chimique des Monnaies Néerlandaises et sur la Volatilisation de l'Argent, by A. D. van Riemsdijk. (Extrait des Archives Néerlandaises, 1868, vol. 3.) This paper contains much interesting information, and is well deserving the attention of directors of mints and assayers.

[5] On the Amounts of Lead contained in some Silver Coins. Proceedings of the American Academy of Arts and Sciences, Sept. 11, 1860, p. 52.

The silver used in the U. S. Mint is reduced from chloride by means of zinc, in a sample of which Eliot and Storer found 1% of lead, and thus they account for the presence of lead in the coin. The silver used at the French Mint is precipitated by copper from an acid solution of sulphate of silver, obtained in the operation of "parting" by sulphuric acid, to be hereafter described; and as commercial sulphuric acid, contaminated with sulphate of lead, is employed for that purpose, and as, moreover, precipitation is effected in leaden vessels, the presence of lead in the French silver coin is, they think, sufficiently explained. They conjecture that the silver of the English coin of 1816 was the product of cupellation, and that the lead had not been wholly removed. The silver of the Spanish and Mexican dollars was extracted by the Mexican amalgamation process, in which lead is not in any way employed. The occurrence of lead in small proportion in ancient silver coins has also been noticed. Brüel found lead in six analyses of such coins of the reigns of Vespasian, Trajan, Hadrian and Faustina Junior, the extremes being 0·02% and 0·12%;[6] and Professor Draper found nearly 3% of lead in a silver coin of Hadrian.[7]

According to F. Pisani, the presence of silver in commercial lead may be immediately detected by dissolving it in nitric acid, leaving the liquid to cool, and adding a little iodide of starch. The only precaution necessary is to saturate the excess of acid with carbonate of lime, to avoid action upon the iodine. Silver-salts immediately decolorize iodide of starch, but the salts of lead and copper have no action upon it. When the metals which decolorize iodide of starch are brought to their maximum of oxidation by nitric acid, only silver and mercury retain this property. The action of these metals is easily understood, when we consider their great affinity for iodine. Iodide of starch, agitated with chloride of silver, yields its iodine and converts the metal into iodide. The filtered liquid contains chlorine, and the colour disappears. Iodide of starch is the most sensitive reagent for detecting silver, provided mercury be not present. Thus it is sufficient to add $\frac{1}{8}$ of a cub. centim. of iodide of starch to 100 c. c. of a liquid containing $\frac{1}{10}$ milligrm. of silver to cause immediate decolorization; the same quantity of iodide of starch gives a very perceptible colour to 100 c. c. of pure water. In a liquid of less volume $\frac{2}{100}$ milligrm. of silver may be detected.[8] It is not, I think, probable that this method of detecting silver in lead will be adopted in preference to other analytical processes.

Melting of standard silver.—At the Mint in London, standard silver was formerly melted in circular pots or crucibles of wrought-iron, 12 in. in diameter at the mouth, but widening towards the bottom, which is rounded, and 15 in. deep (inside measure). A pot weighed

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[6] Resultate der chemischen Untersuchung alter Münzen durch Hrn. Münzwardein [literally Mint-warden;—Master of the Mint]. Brüel zu Hannover. Karsten's Archiv, 1844. 18. p. 505.

[7] Eliot and Storer's paper, antea cit. p. 62.

[8] Compt. rendus, Dec. 15, 1856, p. 118, quoted in the Chemical Gazette, 1857, 15. p. 84.

about 180 lbs., held 5000 ozs. of silver, which was the fullest charge, and served for melting 40 or 50 charges. Plumbago crucibles are now used at the Mint: they are 11 in. in diameter at the mouth, but contract towards the bottom, which is rounded, and are 13½ in. deep (inside measure). A pot weighs about 44 lbs., holds 4000 ozs. of silver, and serves for melting about 12 charges. A full charge requires 2 hours for its fusion. In heating the furnaces and melting 12 charges, which constitute a day's work, from 20 to 24 bushels of coke are consumed. As a certain quantity of coke is left at the end of the day and is used in the next day's work, the quantity of coke consumed per charge should be deduced from the lower number, which quantity amounts to 1·67 bushel.

Wrought-iron melting-pots were formerly used in the Mint of Paris for making the standard silver alloy for coinage, consisting of 900 parts by weight of silver and 100 of copper per 1000 of alloy. They were capable of holding more than 700 kilogrammes, but usually not more than 650 were melted in them (*i.e.* of the value of 130,000 francs). The first melting lasted from 5 to 6 hours, and the succeeding ones 3 hours each. From 30 to 40 meltings might be made in the same pot, and in rare cases as many as 50. The molten metal was laded into the ingot-moulds by means of iron ladles.[9]

SILVER-SOLDERS.

By silver-solders are meant especially alloys containing silver, used for soldering articles consisting either of silver, or of alloys of silver.

English silver-solders.—There are several kinds of such solders, of which the composition is stated by Holtzapffel to be as follows:[1]—

I. Hardest[2] silver-solder:—Fine silver 4 parts, copper 1 part; it is said to be difficult to melt, and occasionally used for "figures."

II. Hard silver-solder:—Sterling silver 3 parts, brass-wire 1 part, which is added when the silver is melted. [The brass of which brass-wire is made, consists of about 2 parts of copper and 1 part of zinc.]

III. Soft silver-solder:—Fine silver 2 parts, brass-wire 1 part. It is stated that some silversmiths add also ¾ part of arsenic in order to render the solder whiter and more fusible, but that the malleability of the solder is thereby diminished.

Silver is also soldered with an alloy of 2 parts of tin and 1 part of lead, and with pure tin.

My friend Mr. Edward Matthey, of the firm of Johnson, Matthey, & Co., has obliged me by consulting a trustworthy working silversmith, with reference to the foregoing information, and has reported to me that it is correct. Concerning No. III., Mr. Matthey states that it is "a very nice white solder, and is used for ordinary plate-

[9] Chaudet, L'Art de l'Essayeur, 1835. p. 355.

[1] Turning and Mechanical Manipulation, etc. By Charles Holtzapffel. 1843. 1. p. 283.

[2] The terms *hard* and *soft* are used to indicate relative fusibility.

work," and that he "has heard of arsenic being put in when there is any delicate work to be done." He has prepared a specimen of each of the solders above described since I applied to him for information on the subject (August 1876).

A solder suitable for jewelry and of the following composition is mentioned by Tenner ;[3] and as English weights are given, it may be inferred that this solder is used in England :—

	Dwts.
Fine silver	19
Copper	1
Brass	10

Other solders are reported to be made by melting 3 parts of silver with 7 parts of copper, and 4 parts of silver with 6 parts of copper.[4]

French silver-solders.—An alloy, which is used in France for soldering silver wares of the standard of 950, has, according to Chaudet, the following composition per 1000 :[5]—

Silver	666·67
Copper	233·33
Zinc	100·00
	1000·00

In making this solder, the zinc should be alloyed with twice its weight of copper, so that the weights of materials directly employed will be as under :—

Silver	666·67
Brass (containing 33·3% of zinc)	300·00
Copper	33·33
	1000·00

According to Guettier, the solders II. and III., described under the head of English silver-solders, and also the following solders, are used in France :—

	Parts by weight.				
Silver	5	2	4·00	2·0	1
Brass	1	–	—	—	–
Bronze (*i.e.* copper 90%, tin 10%)	–	1	3·00	—	1
Arsenic	–	–	0·25	0·5	–
Copper-foil (*clinquant*)	–	–	—	1·0	1
	6	3	7·25	3·5	3

When arsenic is used, it is not added until after the fusion of the other metals. In order that the solders should be homogeneous, Guettier asserts that they should be re-melted several times. To fit them for use they are rolled or hammered into thin strips, and then

[3] Handbuch der Metall-Legirungen, 1860. p. 114.
[4] Gray's Operative Chemist, p. 711. London, 1828.
[5] Chaudet, op. cit. p. 380.

cut with shears into small bits, so that they may, in admixture with borax, be applied to the parts intended to be soldered together. Their fusibility decreases as the proportion of silver in them decreases. When repeated solderings are made upon the same article, it is necessary to use them successively in the order of their fusibility, beginning with the least fusible, so as not to re-melt the solder previously applied. [But this precaution is surely not required except in the case of small articles or only in large ones when the successive solderings occur near the same place.]

German silver-solders.[7]—For soldering silver and plated articles, the following hard solders made of silver and brass are used :—

I. For silver wares containing $\frac{15}{16}$ and upwards of fine silver, the alloy is made of 3 parts by weight of fine silver with 1 part of brass.

II. For silver wares containing $\frac{13}{16}$ of fine silver, the alloy is made of 2 parts of fine silver with 1 part of brass.

III. For silver wares containing *less* than $\frac{13}{16}$ of fine silver, the alloy is made of 1 part of fine silver with 1 part of brass; or an alloy is used prepared from a mixture of 3 parts of zinc and 16 parts of silver plate (consisting of 12 parts of fine silver with 4 parts of copper).

Ancient silver-solders.—Theophilus, *alias* Rugerus, priest and monk, in his treatise on Various Arts, written early in the eleventh century, has described the process of soldering silver. As far as I can interpret his description, silver-solder was composed of 2 parts of pure silver and 1 part of copper, both in the state of fine filings, but not previously melted together. The flux used therewith was a mixture of carbonized cream of tartar and common salt, tempered with water to the consistency of paste. He gives minute directions concerning the mode of manipulation.[8]

In 1568, Perez de Vargas published the following account of silver-solders :—The solder richest in silver should consist of 5 parts of silver, 1 part of copper, and $\frac{1}{2}$ part of brass; and, indeed, there ought to be more brass than copper. The solder poorest in silver should consist of 3 parts of silver, 1 part of copper, and $\frac{1}{2}$ part of brass.[9]

In 1635 Bate published the following directions for preparing silver-solders :—"*Hard Soder* (*sic*) *is thus made :* take a quarter of an ounce of silver and a three penny weight of copper, melt them together, and it is done. *Soft Soder is thus made :* take a quarter of an ounce of silver and a three pennyweight of brasse, melt them together, and it is done."[1]

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[6] Guide pratique des Alliages métalliques. Par A. Guettier. 1865. pp. 324–326.

[7] Handwörterbuch der Chemie, 1859. 7. p. 959.

[8] An Essay upon Various Arts in three Books, by Theophilus, called also Rugerus, Priest and Monk. Translated, with notes, by Robert Hendrie. 1847. p. 241.

[9] Traité singulier de Métallique, etc. French translation from the Spanish. 2. p. 172.

[1] The Mysteries of Nature and Art. 2nd edit. Printed for Ralph Mabb, 1635. p. 256.

ANCIENT SILVER COINS.

Some information on this subject may not be without interest. Roman silver coins of the first three centuries were found at Baden-Baden in 1825, and analysed by Walchner of Carlsruhe, with the following results:[2]—

Name of the Emperor when coined.	Per cent. Silver.	Copper.
Domitian	86·134	13·866
Trajan	89·016	10·984
Hadrian	88·235	11·765
Antoninus Pius	91·331	8·669
Marcus Aurelius	63·259	36·741
Commodus	79·726	20·273 (*sic*)
Septimius Severus	54·698	45·302
Caracalla	51·258	48·742
Heliogabalus	50·566	49·434

The second, third, and fourth coins in the list had nearly the same standard as most modern silver coins.

SILVER AND ZINC.

According to Berthier the alloys of silver and zinc, which contain a large proportion of zinc, are bluish-white, brittle, and granular in fracture. It has been stated that an alloy consisting of 11 parts by weight of zinc and 1 of silver is wholly volatilizable; and in order to test the truth of such statement, Berthier heated to 60° (Wedgwood's pyrometer) a mixture, composed of 5 grammes of silver in powder, 3 of oxide of zinc, and 12 of black flux, until all appearance of volatilization had ceased. There remained a button of metal, which weighed 5·95 grammes, and consisted of 80% of silver and 20% of zinc, so that about $\frac{1}{6}$th of the silver had been volatilized. This button was rolled out into very thin leaf, which was rigid, elastic, very tenacious, and capable of being bent several times backwards and forwards without breaking.[3]

The following observations on the alloys of silver and zinc were made by my friend Mr. G. H. Godfrey (formerly Hochstätter), in my laboratory in 1870.

To 600 grains of zinc, kept molten in a crucible as near the melting-point of the metal as practicable, 12 grains, *i.e.* 2 per cent., of finely granulated silver were added. After the lapse of half an hour, the contents of the crucible were poured out, when it was found that almost the whole of the silver remained in its original solid state at the bottom. The fracture of the metal poured out resembled that of ordinary zinc, and it contained not more than 0·175 per cent. of silver. Hence it appears that under the condition of temperature above mentioned zinc exerts only a slow solvent action on silver. On the other hand, it was ascertained that at higher temperatures alloys of silver and zinc are readily formed.

[2] Schweigger's Jahrbuch der Chemie und Physik, 1827. 21. p. 204.
[3] Tr. des Ess. 2. p. 798.

The following alloys were subsequently produced:—I. was prepared by keeping a mixture of 600 grains of zinc and 60 grains of silver, both granulated, heated at strong redness under charcoal for half an hour; II., III., and IV. were prepared by pouring molten zinc into molten silver, when violent action occurred; in each case the alloy was cast in an ingot-mould:—

	I.	II.	III.	IV.
Silver	8·16	22·47	49·72	67·58
Zinc	91·84	77·53	50·28	32·42
	100·00	100·00	100·00	100·00
Sp. gr.	7·44	7·62	8·61	9·30

I. The surface of the ingot was bluish-grey. The metal was hard, easily frangible, and easily scratched by a knife; its fracture was bluish-grey, finely granular, feebly lustrous, and with the aid of a lens bright specks were seen to be diffused throughout. During the experiment much of the zinc was volatilized; and, on comparing the proportion of silver employed with that in the product, it will be seen that silver in notable quantity must also have escaped.

II. The surface of the ingot was bluish-grey; the metal was harder than in I., easily frangible, but less easily scratched by a knife; its fracture was bright, bluish-grey, and fibro-columnar.

III. The surface of the ingot was copper-red immediately after solidification; the metal was very hard, yet very brittle and easily pulverized; the colour of its fracture, when broken cold, was white and very bright, but when broken hot, it immediately acquired a yellow, red, purple, or blue tarnish, according to the temperature; the fracture was somewhat foliated and columnar, but inclining to conchoidal.

IV. The surface of the ingot had a faint reddish-yellow tint; the metal was hard, and easily frangible; its fracture was at first white and very bright, but in time acquired a yellow tarnish; it was columnar.

An alloy of 2 parts by weight of zinc and 1 of silver, *i.e.* 33·33% of the latter, is stated to be ductile, finely-granular in fracture, and nearly as white as silver.[4]

Péligot has investigated alloys of silver and zinc with reference to their fitness for coinage. He prepared such alloys by dropping the zinc wrapped up in paper into the molten silver, and stirring with an iron rod. He has described the properties of alloys containing 5, 10, and 20 per cent. of zinc respectively. They were all white, but compared with pure silver slightly yellowish. These alloys were much more fusible than the silver and copper alloys of corresponding percentage composition. They could be rolled, and, when hardened by this operation, could be quickly annealed. Coins made of them were elastic

[4] Handwörterbuch der Chemie, 7. p. 958.

and sonorous. Alloys prepared in the ratios Ag + Zn [2Ag + Zn], *i.e.* silver 76·9% and zinc 23·1%, and 2Ag + Zn [4Ag + Zn], *i.e.* silver 86·9% and zinc 13·1%, were pretty malleable; but alloys in the ratios Ag + 2Zn [Ag + Zn], *i.e.* silver 62·4% and zinc 37·6%, and 2Ag + 3Zn [4Ag + 3Zn], *i.e.* silver 68·9% and zinc 31·1%, were too brittle to be rolled. Alloys of silver and zinc are not so easily blackened by sulphuretted hydrogen as the silver and copper alloys of corresponding percentage composition. Péligot found that an alloy consisting of 80 per cent. of silver and 20 per cent. of zinc retains its white colour even when immersed in solutions of alkaline sulphides.[5] It is reported that this alloy has been employed by Doppler for mirrors.[6]

Alloys of Silver, Copper, and Zinc.

The following observations on this subject are also due to Péligot. He prepared alloys composed as under:—

Silver	90	80	83·5
Copper	5	10	9·3
Zinc	5	10	7·2
	100	100	100·0

These alloys were whiter and more malleable than alloys of silver and copper containing the same proportions per cent. of silver, respectively. Péligot remarks that the use of zinc in silver alloys deserves attention, because it costs so much less than copper.[7]

Silver and Lead.

No alloy of these metals is now used in the arts; but Perez de Vargas, the author of a work on metals, etc., dated 1568, states that excellent mirrors were then made of an alloy consisting of 2 parts of silver and 1 part of lead; and that a vessel of copper and even of iron might be silvered by means of such an alloy.[8] The presence of lead in small quantity lessens the malleability of silver. Molten lead dissolves silver, just as mercury does. The sp. gr. of alloys of silver and lead is stated to be less than that of the

[5] Comptes rendus, 1864. pp. 645 et seq.

[6] Watt's Dictionary of Chemistry, 5. p. 287. I have referred to Doppler's paper "Ueber einige wesentlichen Verbesserungen der katoptrischen Mikroskope" (Abh. Böhm. Gesell. 1845–46. 4. pp. 91–128), but have not found any mention therein of the use of such an alloy.

[7] Comptes rendus, 1864. pp. 645 et seq.

[8] Traité singulier de Métallique, etc. Traduit de l'original Espagnol de Perez de Vargas, imprimé à Madrid en 1568. In-12. Par G. G. Paris, 1743. 2. p. 236. This is a remarkable treatise, not, I think, so well known in this country as it ought to be. It contains much interesting and valuable matter concerning the working of metals, niello, enamelling, etc. I have found in it directions for the preparation of type-metal with lead, antimony, and *tin* (v. 2. p. 239). Now the addition of tin to ordinary type-metal is regarded as a modern improvement, and was patented some years ago. The patent became the subject of costly litigation, the result of which might possibly have been affected by the announcement at the time of the fact that this *modern* improvement was known and practised 300 years ago ago!

mean of the two metals.[1] In whatsoever proportions these metals are melted together, *apparently* homogeneous mixtures are obtained; but when certain of these mixtures are cooled in mass, as, for example, in the usual pig-moulds of cast-iron, the composition of the ingots may not be uniform throughout. Cramer in the last century directed attention to the want of homogeneity in argentiferous lead, as is shown by the following extract from his well-known and valuable treatise on Assaying: "whence it plainly appears, that Silver and Lead mixt only by Fire, are not so well mixt to each other, as that a perfectly proportionable Quantity of both may be found in any Part of the Mixture whatever: Which, being either unknown to or neglected by Artificers, deceives them very often."[2] In the same treatise it is also thus stated: "Silver melted with Lead, and left to itself, was not evenly dissolved by the Lead, but the same Portion of the Mixture contained more Silver at Top, and less underneath, and Lead in an inverted Proportion."[3] This question of the non-homogeneity of rich argentiferous lead is one of much practical importance with respect to the estimation of its value; and in proof the following instance may be adduced. Many years ago I examined two pigs of rich silver-lead from South America, of which one weighed 98 lbs. (avoirdupois), and contained, in round numbers, 3000 ozs. (troy) of silver per ton, while the other weighed 93 lbs. and contained, in round numbers, 1800 ozs. of silver per ton. They had been assayed in London, and for that purpose portions had been taken from different parts of each pig. My results did not agree with those of the assayer, though I had also operated upon portions of lead taken from the identical spots where he had selected his; nor in successive cupellations did my own results agree with each other, as I did not prepare a sample by melting all the portions together. The pigs were then returned to the assayer to be re-assayed, and in the second report which he delivered, the proportion of silver stated differed by about 1000 ozs. in one case from that stated in his first report. In the second trial each pig had been melted separately, and a portion of the molten metal taken out for assay; and it is only in this manner that a sample, properly so called,—*i.e.* a specimen accurately representing the average composition of the mass,—can be procured.

It was suggested by the late Mr. Pattinson to the Author that the sawdust, obtained by sawing a pig of lead transversely in two, might probably be accepted as a sample; but in the case of ex-

[1] Guettier, Guide pratique des Alliages, 1865. p. 150.

[2] Elements of the Art of Assaying Metals. Translated from the original in Latin by Cromwell Mortimer, M.D., Secretary to the Royal Society, London. 2nd ed. 1764. p. 237. The passage in Latin is as follows: "Inde autem clare patet, Argentum et Plumbum, solo igne confusa, non ita sibi invicem permisceri; ut in qualibet mixturæ parte amborum perfecte proportionata quantitas sit: qua re incognita, vel neglecta, crebrius decipiuntur Artifices" (Joann Andr. Crameri Elementa Artis Docimasticæ. Editio secunda. Pars II. p. 60. Lugduni Batavorum [Leyden], 1744).

[3] Op. cit. p. 236.

tremely rich argentiferous lead, the only safe course is that which the assayer adopted in his second trial, namely, preparing the sample from the metal while in fusion.

Levol has investigated the question of the composition of ingots, composed of silver and lead in 12 different atomic proportions; but as he operated only upon comparatively small quantities of metal cast in the form of spheres, as in his experiments on the alloys of silver and copper, it may be objected that his results are inapplicable to those which occur on the large scale under dissimilar conditions. Nevertheless, the following condensed statement of those results may at least be interesting in a scientific point of view:[4] —

	Formulæ according to which the alloys were made.	Silver, per 1000 of alloy. Calculated.*	Found.†	Variations in the ingot.‡
I.	10Ag + Pb [20Ag + Pb]	912·5	914·0	7·5
II	6Ag + Pb [12Ag + Pb]	862·0	863·0	14·5
III.	5Ag + Pb [10Ag + Pb]	839·1	840·5	23·5
IV.	2Ag + Pb [4Ag + Pb]	675·9	676·5	49·5
V.	Ag + Pb [2Ag + Pb]	510·5	516·6	66·5
VI.	Ag + 2Pb [Ag + Pb]	342·8	347·5	11·0
VII.	Ag + 3Pb [2Ag + 3Pb]	258·0	262·0	13·0
VIII.	Ag + 4Pb [Ag + 2Pb]	206·8	206·0	6·5
IX.	Ag + 10Pb [Ag + 5Pb]	94·4	..	19·5
X.	Ag + 15Pb [2Ag + 15Pb]	65·0	67·25	7·5
XI.	Ag + 20Pb [Ag + 10Pb]	49·4	46·00	2·5
XII.	Ag + 100Pb [Ag + 50Pb]	10·3	9·75	0·25

* Silver, per 1000 parts of alloy, calculated from the formula.
† Actual quantity of silver found in assaying a sample of the alloy, prepared by granulation.
‡ Extreme differences in the proportion of silver in different parts of the ingot.

I. The alloy is tolerably white, grey in fracture, but little malleable, and contracts strongly during solidification.

II. This alloy is greyish-white, and is stated to be singularly like platinum in its colour, as well as in its fine-grained fracture; it contracts strongly during solidification, and changes rapidly in moist air.

III. This alloy is greyish-white, grey in fracture, and contracts strongly during solidification. When heated sufficiently with access of air, it acquires a very beautiful violet-blue tint, which is not the same as that assumed by pure lead under the same conditions. At a temperature very near its melting-point, this alloy swells up very considerably into a spongy cauliflower-like mass. Levol gives the following as the composition of such a mass deduced from analyses of several specimens expressly prepared: these specimens are stated to have been constant in composition :—

	Per cent.
Silver	83·13
Protoxide of lead	13·50
Metallic lead	2·30
Loss	1·07
	100·00

[4] Mémoire sur les Alliages, considérés sous le Rapport de leur Composition chimique. 2ième partie. Ann. de Chim. et de Phys. 1853. 3. sér. 39. p. 173.

The chief results relating to this alloy are as follow:—When a certain quantity of solid lead is put into a bath of pure silver, of which the surface is beginning to solidify, there is immediate combination between the two metals; the surface of the bath instantly becomes flat, dull, and wrinkled; and then follows the production of the cauliflower-like excrescence, with the development of heat and light. In order to re-melt this excrescence, a higher temperature is required than would be needed for a purely metallic alloy made according to the formula Ag^5Pb [$Ag^{10}Pb$]; and this is ascribed to the difference of fusibility between lead and litharge. It has been found that this excrescence is not due to "spitting," caused by the sudden escape of oxygen, as, indeed, might be inferred from its containing lead in the metallic state. The phenomenon does not take place when molten silver, containing oxygen in solution, is poured into molten litharge, sufficient to be entirely covered by the latter, and the whole is left to cool. In this case the absorbed oxygen escapes quietly, and there is no "spitting," nor is any minium formed. The explanation, which Levol suggests, is little, if anything more, than an expression of the fact.

IV. This alloy is tolerably malleable, and may be flattened or rolled out, but it has only little tenacity; it melts at a temperature approaching cherry-redness; it is bluish grey, and quickly changes in colour by exposure to moist air or sulphuretted hydrogen. According to Matthiessen its sp. gr. is 10·80 at 13·5° C.

Nothing of interest is stated concerning Nos. V. VI. VII. VIII. IX. According to Matthiessen the sp. gr. of No. V. = 10·925 at 10·8° C.; of No. VI. = 11·054 at 12·5° C.; of VIII., 11·144 at 18·2° C. No. VI. is stated to be much more like lead than silver, to be soft, and tolerably ductile and malleable.[4]

X. About 200 grammes of this alloy were melted, well stirred and poured into a U-tube of refractory glass, in which it was kept melted without stirring during an hour, and afterwards left to cool quietly. The proportion of silver in the metal in the curved portion was 26·5 per 1000, and was much greater in that of the two branches, the extremes in the latter being 101·5, 77·5, and 84·0, 63·0, respectively: the distribution of silver in the metal of both branches was very irregular; thus, at the top of one it was 101·5, and at the top of the other 68·5, and in the middle of each it was, respectively, 77·5 and 84·0. Liquation seems to have occurred, but a single experiment, especially where the results are apparently so conflicting, does not suffice to settle this point.

XI. XII. require no special comment, except that the composition of the latter was practically uniform. According to Matthiessen the sp. gr. of No. XI. = 11·285 at 22·2° C. An alloy containing 12·5% of silver, and nearly approaching No. XII. in composition, is described as "white, greyish, a little less ductile than lead

[4] Guettier, Guide pratique des Alliages, 1865. p. 150.

and sensibly less so than silver, and less fusible than pure lead."[6]

Wertheim found that an alloy consisting of 26·36% of silver and 73·64% of lead, *i.e.* Ag+3Pb [2Ag+3Pb], had a sp. gr. of 10·743.[7]

Silver and Bismuth.

It has been stated in the Author's volume on the Metallurgy of Lead, that bismuth might be substituted for lead in the process of cupellation, which could not be done if these metals were unable to form alloys with each other.

The alloy consisting of 50% of each metal, is said to have the sp. gr. of 10·709, and the colour of bismuth; to be brittle, laminar in structure, and not to expand during solidification.

The alloy containing 33·33% of silver is said to be steel-grey, laminar in structure, and to expand during solidification.[8]

The alloy containing 33% of bismuth (*i.e.* Bi+2Ag [idem]), is said by Berthier much to resemble silver in whiteness, to be soft, fragile, yet capable of being flattened a little under the hammer without breaking; and its fracture to be crystalline, and slightly lustrous.[9]

R. Schneider has observed the remarkable fact that when impure bismuth, containing sulphur, arsenic, iron, nickel, cobalt, and silver, is fused and poured upon a cold plate, the globules of metal, which are thrown up during the solidification of the mass, contain at least 99·5% of bismuth; and, of the heavy metals, only silver is found in the globules, the copper remaining entirely in the mass. Schneider suggests that the property in question might be advantageously employed for a preliminary purification of commercial bismuth.[1]

Silver and Thallium.

I am indebted to my friend Mr. Cookes, the discoverer of thallium, for the following information on this subject:—"The two metals readily fuse together, and the resulting alloy is somewhat malleable, but will not bear hammering much. They are easily separated on a cupel; indeed, I have suggested that thallium might be used for cupelling silver, instead of lead." Mr. Crookes presented me with a specimen of an alloy formed by melting together equal weights of silver and thallium. The colour of its surface, freshly scraped with a knife, is white; but it quickly tarnishes and acquires a yellowish tint, due to oxidation of the thallium. When moistened turmeric paper is placed even on its freshly-cut surface, it is immediately stained brown. The alloy is easily cut with a pen-knife.

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[6] Guettier, Guide pratique des Alliages, 1865. p. 150.

[7] Ann. de Chim. et de Phys. s. 3. 1844. 12. p. 388.

[8] Gmelin's Handb. 6. p. 193. The authorities quoted are Muschenbroek and Marx.

[9] Tr. des Ess. 2. p. 799.

[1] Chemical Gazette, 1855. 13. p. 436 quoted from Bericht der Akad. der Wiss zu Berlin, 1855. p. 495.

Silver and Mercury.

The use of the word amalgam is conventionally restricted to alloys of metals with mercury, although there is no etymological or other reason for such restriction. Amalgam is derived from the two Greek words ἅμα, together, and γαμεῖν, to marry; and it is obvious that when molten lead, for example, dissolves and alloys with silver, it is as much a marrying together or union as when mercury dissolves, and alloys with, silver. The only difference is that mercury unites with other metals at common temperatures, because it is liquid at such temperatures, whilst lead is not, and must be liquefied by heat before it can act like mercury. Silver, as just stated, is attacked by mercury at common temperatures; but amalgamation more quickly occurs, say at or near the boiling-point of mercury, especially if the silver be finely divided. According to Daniell, when a bar of silver is kept immersed in mercury during 24 hours, it takes up only a small quantity of this metal, and remains malleable. If, however, the temperature is raised to the boiling-point of mercury, and the whole be gradually cooled, soft needles of amalgam will be deposited on the surface of the bar where in contact with mercury.[2] Silver-amalgam is formed by prolonged contact of mercury with an aqueous solution of nitrate of silver; and in this way the *arbor Dianæ* of the old chemists is obtained, for the preparation of which various receipts will be found in chemical treatises. With too large a quantity of mercury, liquid instead of crystalline amalgam is produced. Berzelius gives the following directions for obtaining crystals of silver-amalgam of the formula $AgHg^3$ [AgHg], *i.e.* of 35% of silver and 65% of mercury. Amalgam, consisting of 7 parts (by weight) of mercury and 1 of silver, is placed at the bottom of a vessel containing a mixture of 3 parts of a saturated solution of silver in nitric acid, with 2 parts of an equally saturated solution of mercury also in nitric acid. In the course of from 24 to 48 hours there will be found in the liquid a multitude of crystals, having a metallic lustre, which extend in the form of ramifications even to the surface of the liquid and constitute the *arbor Dianæ*. The formation of these crystals is due to the precipitation of silver by mercury; and it only occurs when there is more mercury than suffices for the precipitation of the whole of the silver, and less than suffices to dissolve the metallic vegetation.[3]

Joule has prepared silver-amalgams by different processes, and found them to have the following specific gravities and composition:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Specific gravity	14·68	..	..	13·25	12·34	12·49	12·54	11·42
Parts of silver ..	52·6	100·3	115·4	115·2	155·8	106·4	293·3	261·4
Parts of mercury	100·0	100·0	100·0	110·0	100·0	100·0	100·0	100·0

[2] Gmelin's Handb. 6. p. 198, quoted from a paper by J. F. Daniell, Roy. Inst. Journ. 1831. 1. pp. 1–12.

[3] Tr. de Chim. 2. p. 513.

Nos. I.–IV. were obtained by mere contact of mercury with a cold solution of nitrate of silver; Nos. V., VI., with a hot solution of the same salt; No. VII., by the voltaic current; No. VIII. were crystals, which had attached themselves to No. VII. Each of these amalgams was subjected to strong pressure, and found to yield a product of nearly the same composition, namely, of 43·7 parts of silver and 100 of mercury—*i.e.*, of 30·4% of silver and 69·6% of mercury, which Joule considers as a definite amalgam of the formula $AgHg^2$ [AgHg], intermixed with 4·6% of free mercury.[4] Crookewitt had previously obtained amalgams represented by the formulæ Ag^5Hg^{16} [Ag^5Hg^8], $AgHg^2$ [AgHg], $AgHg^3$ [Ag^2Hg^6], and $AgHg^4$ [$AgHg^2$], by keeping different proportions of mercury in contact with an aqueous solution of nitrate of silver.[5] Joule's results lead to the conclusion that there is only one definite amalgam, of the formula $AgHg^2$ [AgHg], and so far there seems to be strong evidence in its favour.

When mercury, which is amalgamated with silver, but not in sufficient quantity to destroy its liquidity and render it solid, is filtered through chamois leather or canvas, aided by pressure such as squeezing with the hand, the silver will remain on the filter in the state of pasty amalgam of approximately definite composition. That, before filtration, such a definite amalgam existed appears probable if not certain; but whether it was actually dissolved or merely mechanically suspended in the mercury separated by filtration are questions which will obviously present themselves, and which it may not be easy to answer with certainty. But the following considerations seem to favour the mechanical suspension view of the case. It is stated that in mercury, which contains silver only in small proportion, the silver-amalgam collects towards the top; whereas in the case of mercury containing gold the opposite occurs. Now the specific gravity of mercury is greater than that of silver-amalgam and less than that of gold-amalgam, which facts agree with the mechanical suspension view, but not with that of actual solution. Malaguti and Durocher found it difficult to procure from a quantity of mercury, containing silver-amalgam, a sample, properly so called, *i.e.* a fraction containing the same proportion of silver as the rest of the mass. In operating by decantation, they remark, it will be found that, according to the extent of surface, the form of the vessel, and especially the configuration of that part of the edge of the vessel over which the metal flows, the fraction separated will contain sometimes a greater and sometimes a less proportion of silver, and will never be of constant richness. The report of the following experiments which they made on this subject deserves, I think, careful attention. They put into a glass vessel 20 grammes of mercury, containing 0·1 gramme of silver or 50 ten-thousandths, and poured out the whole mass, not at once but

[4] Jahresber. 1863. p. 281.

[5] Idem, 1847 u. 1848. p. 393.

at four times successively. Each of these four portions was eva
rated in a porcelain capsule, and the residue heated to redness.
numerical results are shown in the following table :—

Successive portions.	Weight, in grammes, of the mercury poured out.	Weight, in milligrammes, of the silver left after evaporation of the mercury.	Richness of the me in silver expresse 10-1000ths.
1	5·0	71	142
2	5·4	17	34
3	5·0	7	14
4	4·6	5	10
	20·0	100	

It next occurred to Malaguti and Durocher to try to procur
sample by means of a glass tube, plunged to the bottom of a mass
mercury, contained in another and wider tube, so placed that the a
of both tubes should be coincident. But this method proved m
fallacious than the preceding one, which they attributed to in
ference caused by capillary action ; and in order to obviate that sou
of error, they modified the experiment in the following manner. U
a stand, set in the middle of a large flat-bottomed porcelain capsu
they put a plate of ground glass, and upon this plate they put a r
of glass, ground at the edges. Argentiferous mercury was pou
into the ring, and into the mercury they plunged vertically a gl
tube, also ground at the edges,—keeping its axis as much as possi
coincident with that of the ring,—until it rested on the plate of gl
at the bottom. The ring was now raised, when all the mercu
except that retained in the central tube, flowed over the glass pl
into the underlying porcelain capsule. The portion of mercury
collected was weighed, evaporated, and heated to redness.
diameters of the ring and tube were varied, yet the results, wh
differed much, were always more or less unsatisfactory. Fina
Malaguti and Durocher hit upon the following plan, which yiel
results approximating closely to the truth, though not absolut
exact, and which they considered sufficiently satisfactory.
argentiferous mercury is put into a glass tube of about 2 centimet
diameter, and closed at one end. The tube is held in the hand w
the thumb on the mouth, then inverted, and in that position stron
shaken over a large porcelain capsule ; and while the shaking
strongest, a portion of the mercury is allowed suddenly to escape
suitably moving the thumb. By repeating this two or three time
sample is generally obtained not exceeding 7 grammes in weig
About half of this sample is evaporated in a retort, and the remain
in a small porcelain capsule ; and the residues are heated to redn
to drive off the last traces of mercury. The results of ass

conducted as above described are presented in the following table :—

Total weight of the mercury, in grammes.	Silver contained in the mercury, in milligrammes.	Weight, in grammes, of the sample taken.	Silver in the sample, in milligrammes.	Silver, in milligrammes, in the total mass calculated from that in the sample.	Variations, in milligrammes, in the quantity of silver compared with that contained in the original mercury.	
					Excess.	Deficiency.
19·5	100·0	6·0	31·5	102·0	2·0	—
19·5	50·0	5·8	13·5	49·0	—	1·0
19·5	20·0	6·2	6·5	19·9	—	0·1

From these experiments, it appears that errors would only become sensible in the case of amalgams containing 1–400th of silver.[6]

Amalgam used in silver-plating consists of 85% of mercury and 15% of silver. It may be prepared by triturating silver-leaf and mercury together cold; but the process is quickened by heat, and accordingly red-hot particles or small plates of silver may be thrown into heated mercury.[7]

According to Guettier, an amalgam, used for silvering purposes, is made by projecting 1 part of granulated silver into from 12 to 15 parts of mercury heated to 200° C., and filtering and squeezing through chamois leather, by which means the excess of mercury is separated from the amalgam, which remains on the filter.[8]

Mercury is very largely used in the extraction of silver from ores containing sulphide, antimonio-sulphide, arsenio-sulphide, chloride, and chloro-bromide of silver, with frequently metallic silver in addition, the silver in every case being obtained in the state of amalgam, and the processes in which it is so applied are designated by the general expression, "Amalgamation of Silver Ores." Indeed, by far the greater part of the silver produced in the world is obtained by such processes, a description of which will occupy a considerable portion of this volume on the Metallurgy of Silver. The treatment of this subject in a comprehensive manner involves numerous minute, and, it may be, wearisome details, which will be reserved for communication in the sequel; but in this place the following observations may be appropriately introduced.

The experiment above mentioned by Daniell seems to indicate that when a mass of solid silver is immersed in mercury the amalgam formed upon its surface does not only not dissolve at ordinary temperatures in the surrounding mercury, but tends to retard or prevent the amalgamation of the subjacent silver; and this agrees with the conclusion at which Malaguti and Durocher arrived from their

[6] Op. cit. pp. 336–342.
[7] Chaudet, L'Art de l'Essayeur, p. 390.
[8] Guide pratique des Alliages, 1865. p. 151.

experiments, namely, "that there is produced at the surface of the metal a very thin layer of amalgam which arrests the ulterior action of the mercury."[1] Hence, they remark, where gold ore or certain mixed ores of silver and gold are treated directly with mercury, it is usually the practice to grind the mixture of materials, with the addition of a due proportion of water, under mill-stones, instead of causing it to rotate in barrels; because the friction of the former is constantly removing this adherent film of amalgam and exposing fresh surfaces of silver to the action of the mercury.

Not only the quantity, but the nature of the intermixed foreign matter may have a decided influence upon the process of amalgamation, owing to its greater or less adhesiveness to the surface of the silver. Malaguti and Durocher made many experiments upon this subject. They tried the effect of various kinds of foreign matter, under exactly the same conditions as to proportion of silver, quantity of water, mercury, and foreign matter, and time of agitation, and found great differences in the quantities of silver yielded to the mercury. In the following tabular statement is shown some of their results: in each case the weight of the foreign matter was 10 grammes, that of the mercury 13 grammes, and that of the silver 0·1 gramme in the state of chloride (*i.e.* 0·130 gramme of chloride of silver); the whole was mixed with water to the consistence of semi-liquid paste; the rotation, in the same apparatus as elsewhere described in this volume, lasted 20 hours, and the total contact 6 days.[2]

Name of the foreign matter.	Weight of silver yielded to the mercury. Gramme.
Clay	0·0014
Chalk	0·0037
Somewhat argillaceous hydrous oxide of iron	0·0077
Sand	0·0094
Saccharoidal marble	0·0100
Burnt brick	0·0107
Sulphate of baryta	0·0153

In these cases it will be noted that chloride of silver was operated upon, and not directly metallic silver. The chloride was reduced by the mercury, with the formation of calomel and the liberation of metallic silver in a very fine state of division. It may be objected that the resulting calomel might intervene between the reduced silver and the mercury, and so affect the process; but admitting that such intervention occurred, the same condition was present in every instance. Again, it may be urged that the adhesiveness of the foreign matter may not be exactly the same in the case of metallic silver as in that of calomel; but even then there can be little doubt that what sticks most pertinaciously to the particles of the latter, will also stick pertinaciously, though it may not perhaps be in the same degree, to the particles of the former.

The conclusion of Malaguti and Durocher is, that of all the

[1] Op. cit. p. 348.

[2] Op. cit. p. 363.

foreign matters above enumerated the most plastic, namely clay, is that which was accompanied with the smallest yield of silver; whilst the largest yields were obtained in the case of foreign matters "very dense and incapable of imparting a viscous property to the pasty mixture." On the other hand, the presence of minute hard particles, such as siliceous sand, might, it is readily conceivable, tend by their attrition to detach the thin superficial layer of amalgam previously described, and so promote amalgamation.

There are also other conditions which affect amalgamation, such as the consistence of the mixture, the quantity of mercury, rapidity of rotation, temperature, etc.; but these will be more properly considered hereafter in the descriptions of the various processes of amalgamation.

Silver and Platinum.

Lewis, in the last century, experimented upon alloys of silver and platinum, and published his results in a volume, often to be had for an insignificant sum, but rarely appreciated as it ought to be.[3] He prepared and described the following alloys; but, as he only used 10 or 20 grains of platinum in each experiment, the quantity of alloy produced was probably insufficient to furnish thoroughly satisfactory evidence of quality:—

	I.	II.	III.	IV.
Silver.....	1 part	2 parts	3 parts	7 parts.
Platinum.....	1 „	1 part	1 part	1 part.

The mixtures employed in making I., II., and III. required a strong white-heat for their fusion; the products were hard and brittle, in proportion to the amount of platinum which they contained. The ingredients of IV. "melted together pretty easily"; the product "hammered tolerably well, proved much harder than silver, and not so white, nor of so fine a grain." All four products had a yellow tint.

Lewis subsequently made experiments upon 60 grains of platinum "with four times, eight times, twelve times, twenty times, and thirty times as much fine silver," but he has not particularly described the products. He remarks, however, that, "on pouring them into moulds, unless the heat was very intense, a considerable part remained behind, the silver seeming to quit the platina on an abatement of the heat. When the heat was so strong that the whole run fluid into the mould, great part of the platina separated and fell to the bottom on cooling," unless the product solidified immediately. Lewis observed that "numerous metallic globules appeared all over the insides of the crucibles [in which the alloys were made], and many on the covers

[3] Commercium Philosophico-Technicum; or the Philosophical Commerce of Arts: designed as an Attempt to improve Arts, Trades, and Manufactures. By W. Lewis, M.B. and F.R.S. London, 1763. 4to. p. 522. This volume was intended to be followed by others, which, it is greatly to be regretted, never appeared. It contains much information both of scientific interest and of practical value; and if its merits were known, it would, I think, be more in request than it is.

also." In making the alloys he employed various fluxes; viz. borax, black flux, nitre, and common salt: but "the differences in regard to the fluxes, and in the proportions of the two metals, seemed to make no material difference in this respect [*i.e.* the formation of globules]. Some of the mixtures were melted over again, in fresh crucibles, several times; the metal sparkled up in the same manner each time." Lewis does not appear to have ascertained the composition of these globules.

Berthier states that "the alloys of silver and platinum are much less ductile and less white than silver; and that silver is rendered brittle (*aigre*) by 7 per cent. of platinum [which latter statement my friend Mr. Edward Matthey assures me is incorrect]. When the platinum predominates, part of it may be separated by liquation. Nitric acid attacks these alloys and dissolves a considerable quantity of platinum along with the silver. Concentrated sulphuric acid dissolves out the silver, leaving the whole of the platinum in the metallic state. The alloy, consisting of 35·7 per cent. of silver and 64·3 per cent. of platinum, *i.e.* Ag+2Pt [Ag+Pt], melts at 150° (Wedgwood's pyrometer) into a button which in colour is midway between silver and platinum, and flattens under the hammer but breaks in rolling."[4]

An alloy of silver and platinum, containing only 5% of the latter, completely dissolves in nitric acid; but if the platinum much exceeds that proportion, part of it remains undissolved. But in sulphuric acid only the silver dissolves; and when the nitric acid solution of both metals is heated with sulphuric acid, the platinum is separated.[5]

Dentists use an alloy composed of 2 parts by weight of silver and 1 of platinum, and the same alloy has been adopted as a standard of electrical resistance. It is extremely ductile, as I am informed by my friends Messrs. Johnson, Matthey, & Co., who prepare it as an article of commerce.

Silver and Palladium.

Mr. W. J. Cock was, I believe, the first to investigate the alloys of these metals, and to introduce into the arts an alloy consisting of 60 per cent. of silver and 40 per cent. of palladium. This alloy is white, pretty hard, elastic, and malleable, and is not blackened by sulphuretted hydrogen.[6] I found that an alloy containing not more than 25 per cent. of palladium was also not tarnished by that gas. I prepared a considerable quantity of it, part of which I had manufactured into a set of weights, which now for nearly thirty years have remained as bright as at first. Another part of it I had rolled into sheet and converted into powder by Mr. Lane, goldbeater and bronze-powder manufacturer of Birmingham; and the late Mr. Herbert Minton, proprietor of the China Works at Stoke-upon-Trent, obliged me by

[4] Tr. des Essais, 2. p. 800.

[5] Handwörterbuch der Chemie, 7. p. 958.

[6] Memoirs of the Chemical Society of London, 1843. 1. p. 163.

trying it on china by firing in the usual way. The metal adhered well, and acquired a fine polish by burnishing; but its colour was inferior to that of silver. Wertheim found that the sp. gr. of an alloy, formerly used by dentists, consisting of 38·1% of silver and 61·9% of palladium, was 10·903.[7] [The proportions here stated should, I think, be reversed.] When silver containing palladium is dissolved in nitric acid, some of it passes into the solution.

Silver and Iridium.

My friend Mr. E. Matthey, of the firm of Johnson, Matthey, & Co., has informed me that there is no alloy of silver and iridium; and that, after exposing a mixture of these metals to a high temperature, on attempting to pour out the contents of the crucible, silver alone flows out, and a thick mass is left in the crucible. No metallurgists, I believe, have had so much experience in the practical treatment of iridium as the firm in question.

Silver and Tin.

According to Berthier, these alloys have about the same colour as pure silver, are brittle or semi-ductile, and in general hard; that containing 20 per cent. of silver being nearly as hard as bronze. The smallest trace of tin imparts brittleness (*aigrit*) to silver. These alloys are very oxidizable. On heating them with corrosive sublimate, the tin volatilizes in the state of chloride, and the silver is left pure. An alloy composed of 48 per cent. of silver and 52 per cent. of tin, *i.e.* Ag+2Sn [Ag+Sn], is flattened under the hammer, and may be rolled into thin sheets, which, however, are ragged at the edges, and break with the least effort on attempting to fold them.[8] The sp. gr. of alloys of silver and tin is less than that of the mean of the two metals.[9] Wertheim found that an alloy consisting of 6·34% of silver and 93·66% of tin, *i.e.* Ag+28Sn [Ag+14Sn], had a sp. gr. of 7·494.[1] Dentists use the filings of an alloy consisting of 60% of silver and 40% of tin, in admixture with mercury for stopping teeth.

Silver and Iron.

This subject has been treated by the Author in a previous volume on the Metallurgy of Iron and Steel: but it is doubtful whether any alloy, properly so called, of these metals can be formed.

Silver and Manganese.

Berthier endeavoured to prepare an alloy of silver and manganese by heating to 150° (Wedgwood's pyrometer) in a brasqued (*i.e.* charcoal-lined) crucible, a mixture of 13·5 grammes of fine silver in

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[7] Ann. de Chim. et de Phys. s. 4. 1844. 21. p. 595.
[8] Tr. des Essais, 2. p. 798.
[9] Guettier, Guide pratique des Alliages, 1865. p. 149.
[1] Ann. de Chim. et de Phys. 3. s. 1844. 12. p 591.

powder, 8·0 of pure red oxide (*oxide rouge*) of manganese, Mn^3O^4 [idem], 1·0 of charcoal, and 0·5 of melted borax. He obtained a metallic button, perfectly melted, and covered with a slight pellicle of olive-green vitreous slag; it weighed 17·90 grammes, from which he inferred that it consisted of 76·3% of silver and 23·7% of manganese, *i.e.* Ag+Mn [2Ag+Mn]. It was white, inclining to grey, tenacious, and malleable; it could be flattened out under the hammer without breaking, and even rolled out into thin leaves, which, however, were rigid, and either broke or cracked when doubled upon themselves; it was granular and scaly in fracture, and when breathed upon it exhaled the odour of impure hydrogen.[2]

Silver and Nickel.

Berthier published the following observations on this subject. Silver has a sensibly greater affinity for nickel than for cobalt. He heated to 60° (Wedgwood's pyrometer) a mixture of 5 grammes of silver in powder, 1 of pure oxide of nickel, and 16 of black flux, and obtained a well-melted button weighing 5·78 grammes, which consequently contained the whole of the nickel used, and consisted of 86·5% of silver and 13·5% of nickel. It was white, but slightly grey, capable of acquiring a very fine polish, and very magnetic; it rolled well into very thin sheets, which showed no cracks at the edges, and might be folded upon each other several times without breaking, but which were more rigid and less tenacious than pure silver. On heating a mixture of 13·501 grammes of silver in powder and 9·29 grammes of pure oxide of nickel in a charcoal-lined crucible to 150° (Wedgwood's pyrometer), Berthier got a well-melted but non-homogeneous button, weinging 20·85 grammes; by the blow of a hammer it was broken in pieces, of which some had the appearance of pure silver, while others were grey and almost lustreless. The former were slightly magnetic, very ductile, and contained only a few hundredths of nickel: the latter were strongly magnetic, flattened under the blow of a hammer but broke in rolling, and consisted of nickel containing only a few hundredths of silver.

Silver, Copper, and Platinum.

Alloys of silver, copper, and platinum are employed, but to a very limited extent, in certain articles of jewelry and "horlogerie;" and also an alloy of silver, copper, gold, and platinum, which resembles the commercial article known under the name of *doré*.[4]

Silver, Copper, Tin, and Gold.

An alloy of silver, copper, tin, and gold, may be readily formed and produces a firm, solid, and durable metal. It is found in some ancient coins and medals.[5]

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[2] Tr. des Ess. 2. p. 794.
[3] Idem, p. 795.
[4] Guettier, Guide pratique des Alliages, 1865. p. 152.
[5] Idem, p. 152.

Silver, Copper, Tin, and Arsenic.

An alloy of silver, copper, tin, and arsenic, has been tried for the mirrors of telescopes; but, like many other alloys made for the same purpose, it has not answered so well as was expected.[6]

Silver, Copper, and Nickel.

De Ruolz and De Fontenay have patented[7] the production of an alloy, which, they allege, may be employed for almost all purposes to which silver is usually applied.[8] The alloy is composed of silver, nickel, and copper: the following proportions are prescribed:—Silver, 20 parts; nickel, from 25 to 31 parts; and the rest up to 100 parts of copper.[9] It is stated to be advantageous, first, to melt the copper and nickel together in the granulated state, and afterwards to add the silver; charcoal and borax, both in the state of powder, are to be employed as the flux; and the ingots produced are to be rendered malleable by heating for a considerable time in powdered charcoal.

A second patent[1] was obtained for the introduction of phosphorus into the same alloys. Granulated "phosphuret of copper" is to be melted with copper and nickel, and the silver added to the molten mass. The quantity of phosphuretted copper employed should be such as to produce an alloy containing from 0·01% to 0·20% of phosphorus. The alleged advantages of the addition of phosphorus are, that the fusibility of the alloy is increased; the molten metal rendered very liquid; and castings are produced free from porosity, closer in grain, more homogeneous, and whiter. The phosphorus, however, it is stated, greatly lessens the ductility and malleability of the metal: when it is requisite to restore these properties, the phosphorus may be almost wholly eliminated by exposing the metal during a long time "to a cherry-red heat, in a close vessel, with powdered charcoal."

Agreeably to a pretty general practice amongst patentees, the claim in the specification is made as comprehensive as possible, and includes alloys of the above-named metals in *any suitable proportions!* The method of eliminating the phosphorus would perhaps be found more simple than efficient.

Silver, Copper, Zinc, and Nickel.

Since 1852, monetary alloys, consisting of these four metals, have been coined and circulated in Switzerland. There are three denominations of such coins, containing 15%, 10%, and 5% of silver

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[6] Guettier, op. cit. p. 153.
[7] Specification, A.D. 1853. No. 3026.
[8] Chemical Gazette, 1855. 13. p. 238.
[9] The proportions are taken from the Chemical Gazette; according to the specification of the patent, the proportions to be used are:—Silver, 20 parts; nickel from 30 to 75 parts; and copper, from 70 to 75. (See the volume of Abridgments of Specifications relating to Metals and Alloys, except Iron and Steel, p. 246.)
[1] Specification, A.D. 1854, No. 2063.

respectively.[2] The composition of the last-named alloy is as follows:—

	Per cent.
Copper	55
Zinc	25
Nickel	15
Silver	5
	100

Mr. Alexander Parkes, of Birmingham, patented, in 1844, the use of alloys of the following composition per cent.:[3]—

Silver	20	.....	10
Nickel	20	.....	10
Copper	60	.....	60
Zinc	—	.....	20
	100		100

Silver, Nickel, Cobalt, and Iron.

M. Germain Barruel obtained, from a South American silver ore, an ingot of metal of brilliant whiteness (*blancheur éclatante*), yet so hard that he was induced to have knife-blades and a file made of it, which, he states, showed "great resistance." Its composition was as follows:—

	Per cent.
Silver	99·40
Iron	0·35
Cobalt	0·20
Nickel	0·05
	100·00

He reproduced the alloy, and also made other alloys, varying the proportions of the iron, cobalt, and nickel, and thereby either increased or lessened the hardness of the metal.[4]

Silver and Chromium.

Berthier tried in vain to alloy these metals together; and no other person, so far as I know, professes to have succeeded in doing so.

Silver and Tungsten.

The following experiment was made by Berthier:—A mixture of 27·03 grammes of silver and 7·53 of tungstic acid, WO^3 [idem], *i.e.* 4Ag : W [8Ag : W], or 82% of silver to 18% of tungsten, was heated in a brasqued crucible to 150° (Wedgwood's pyrometer).

[2] J. C. Nelkenbrecher's Allgemeines Taschenbuch, 1858. p. 166.

[3] Specification, A.D. 1844, No. 10,366.

[4] Compt. rend. 1852. 35. p. 759.

There remained a button of metal, which is described as well melted, but hollow, and containing in the interior a great number of small isolated shots. The compact portion was rolled out into extremely thin leaves, which showed no cracks, and could be doubled upon themselves without breaking, but they were more elastic and rigid than silver, yet equally bright white.[5]

I endeavoured to alloy silver and tungsten together (1844). At the bottom of a Cornish crucible were placed 100 grains of tungsten, prepared from tungstate of ammonia, next 300 grains of fine silver, and lastly charcoal. The crucible was closed with a luted cover, and heated in a Sefström's blast-furnace with coke for fuel. A button of metal was obtained, which weighed 398 grains. The surface did not appear to have been well melted, and there were many small globules adhering to it. The button was re-melted in the same furnace, and a fruitless attempt was made to cast it into an ingot-mould, as it could not be wholly poured out. Its colour resembled that of standard silver, and it was pronounced by a practical silver-refiner to be sufficiently tough. It was, doubtless, only a mechanical mixture, such as is produced by heating copper and tungsten together in a similar manner.

Silver and Molybdenum.

From an experiment with small quantities, Berthier concluded that molybdenum behaved towards silver like tungsten.[6]

Silver and Potassium.

It is stated that an alloy is formed by melting the two metals together; and that when silver is melted with potash and charcoal, it frequently contains potassium. But the truth of this latter statement is denied by Serullas.[7]

Silver and Sodium.

The following observations on this subject have been made in my laboratory by H. Louis (1876):—An alloy of these metals is produced when sodium, in small pieces, is dropped upon heated silver; and the union is not attended with incandescence. Such an alloy was made in a glass tube by adding sodium until a product fusible below redness was obtained. It was malleable and sectile, and when exposed to the air speedily became incrusted with soda. When heated in the air, it took fire and burned, the sodium being oxidized and silver left in the metallic state. Thrown into water, it ignited, occasionally with explosion, and silver was separated either in small scales or sometimes in small fused globules. The alloy was found to consist of 36·32% of silver and 63·68% of sodium.

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[5] Tr. des. Ess. 2. p. 793.
[6] Idem, p. 794.
[7] Handwörterbuch der Chemie, 1859. 7. p. 952.

Silver and Aluminium.

The alloys of silver and aluminium have been examined by MM. Charles and Alexandre Tissier, manufacturers of aluminium, who have published a treatise on this metal, from which the following information is derived.[3] They state that the alloy containing 4·75% of silver is more elastic and harder than aluminium, susceptible of polish, and as malleable as the latter metal; and that they have disposed of such an alloy for industrial purposes in sufficiently notable quantity to justify these statements. Aluminium alloyed with 10% of silver is no longer malleable. All the alloys of these metals are more fusible than aluminium, fusibility increasing with the proportion of silver. The alloy containing 33·33% of silver is fusible enough to be used as solder, but it runs with difficulty and produces a brittle soldering. It is stated that aluminium alloyed with 3·0% of silver has a very fine colour, and is not acted upon by sulphuretted hydrogen, and that an alloy consisting of equal parts by weight of silver and aluminium is as hard as bronze.[4] The presence of silver in aluminium may be detected by the action of a moderately strong solution of caustic potash, which blackens the surface, owing to aluminium being dissolved and silver left; whereas pure aluminium is whitened by the same treatment.

A. Lange uses an alloy of 100 parts by weight of aluminium and 5 parts of silver for watch-springs. Thin wire of this alloy is rolled, ground (*geschliffen*), and heated in steel moulds until it acquires a light-blue colour. Such springs are stated to be very elastic, hard and light, not so brittle as steel, and not to rust.[1]

Silver and Magnesium.

Many of the alloys of magnesium have been examined by Parkinson in my laboratory, and amongst them two alloys of silver, one containing 10% and the other 20% of silver. The former is yellowish white, and finely granular; the latter is bluish white, and coarsely crystalline: both are harder than magnesium and tarnish slowly.[2]

Other Alloys of Silver.

Alloys of silver and gold will be considered in a subsequent volume by the Author on the Metallurgy of Gold, etc. I have not met with the record of any satisfactory information concerning alloys of silver and glucinium, barium, strontium, calcium, titanium, rhodium, osmium, vanadium, tantalum, etc.

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[3] L'Aluminium et les Métaux alcalins. Recherches historiques et techniques sur leurs Propriétés, leurs Procédés d'Extraction et leurs Usages. Paris, 1858. p. 173.

[4] Handbuch der Metall-Legirungen, by J. Tenner, 1860, p. 27, quoted from Le Technologiste, Janv. 1857, p. 178.

[1] Jahresber. 1874. p. 1077.

[2] See Journ. of the Chem. Soc., March, 1867.

ORES OF SILVER.[1]

Native Silver.

It occurs crystallized in the cubical system; capillary, filiform, or dendritic, forms resulting from the aggregation of minute cubes and octahedra; in laminæ, disseminated, and massive. It is usually the associate of other ores of silver. The composition of native silver seems to have been imperfectly investigated; and of the recorded analyses of it, some, which have been accepted without question and repeatedly published, are unsatisfactory. Thus, Berthier examined a specimen of native silver from a quarry at Curcy, and inferred that it consisted of 90% of silver and 10% of copper, from its losing 10% by cupellation and dissolving in nitric acid with the production of blue colour.[4] He remarks that "it is very singular the composition should be exactly the same as that of silver coinage." Is it possible there may have been a mistake as to its origin? Field analysed "a natural alloy of silver and copper," stated to have come from a mine at about 20 leagues east of Coquimbo, in Chile, and 6 from the Cordilleras. It was "perfectly free from oxygen, sulphur, etc., having exactly the appearance of an artificially smelted product from a copper-furnace." A bit taken from the centre of a large mass consisted of 98·91% of copper and 1·09% of silver, but the proportion of silver was very variable: a piece cut from the surface with a chisel, and which had "almost a whitish appearance," consisted of 92·4% of copper and 7·6% of silver. This superficial silver, it is added, has frequently caused great disappointment amongst the miners, as it falsely indicated great richness.[5] According to Field, when native silver occurs in association with the chloride, chloro-bromide or iodide of silver, as it frequently does in the mines named Colorado and Delirio, near Copiapó, in Chile, it is *perfectly* pure, and when fresh from the mine is "beautifully lustrous and splendid;" but when it occurs in association with arsenical or antimonial minerals, it nearly always contains arsenic or antimony.

John analysed native silver from Johanngeorgenstadt, and found it to consist of 99% of silver and 1% of antimony, with a trace of copper and arsenic.[6] Mr. David Forbes has analysed a nugget of native silver from Chuquiaguillo, in Bolivia: it had been mistaken for platinum; its weight was 100·83 grains and its sp. gr. 10·77 at 14·4° C.; and it had irregularly disseminated through it patches or

[1] The books which have been my chief sources of information in writing the following description of the Ores of Silver, are An Elementary Introduction to Mineralogy, by the late William Philips, new edition, by H. J. Brooke and W. H. Miller, London, 1852; Handbuch der Mineralchemie, von C. F. Rammelsberg, 1860; and A System of Mineralogy, by J. W. Dana, aided by G. J. Brush, 1868. When it may be necessary to refer specially to these works the abbreviations B. and Miller, Ramm., and Dana, will be used respectively. The crystallographic nomenclature of Miller will be used.

[4] Ann. des Mines, 1825. 11. p. 72.

[5] A paper by Field, on this "natural alloy," will be found in the Quarterly Journal of the Chemical Society, 2. p. 29.

[6] Chem. Untersuch., 1. p. 283, quoted from Jameson's System of Mineralogy, 1820. 3. p. 71.

spots of black sulphide of silver.[7] Two analyses were made, and the results are as under :—

Composition of Native Silver.

Silver	97·84	....	97·98
Gold	0·28	....	0·22
Sulphur	0·75	....	0·79
Insoluble residue (nearly pure silica) ..	1·13	....	1·01
	100·00		100·00

Forbes also states that the native silver of Kongsberg, in Norway, contains 0·4% of mercury.[8] (See, further on, the article on Silver Amalgam.) Domeyko states that it is not uncommon to find a few thousandths of mercury in the native silver of Chile.[9] The most celebrated locality of native silver in Europe is that of Kongsberg, where the metal occurs in veins traversing mica-slate and hornblende-slate; it is accompanied by argentite, AgS [Ag^2S], red-silver ore (rare), chloride of silver (rare), galena (usually containing under 1 loth per quintal = 0·03% of silver), brown blende, copper-pyrites, iron-pyrites, magnetic pyrites, native gold, auriferous silver, and native arsenic (frequently mixed with metallic silver); the vein-stones are calc-spar, fluor-spar, heavy-spar, and quartz.[1] The following instances of the extraction of single lumps or masses of native silver from the Kongsberg mines are worthy of note: in 1628, a mass of 68 lbs. (avoirdupois) from the Segen Gottes mine,—in 1630, one of 204½ lbs. from the same mine,—in 1666, one of 500 lbs. from the Nye-Forhaabing mine, which is in the Royal Museum at Copenhagen,—in 1695, one of more than 118 lbs. from the Neue Juels mine,—and in 1769, one estimated at 500 lbs. from the Gottes Hülfe in der Noth mine. Daubrée reports that one mass of native silver was found which weighed 697 kilog. = 1537 lbs. avoirdupois. Two masses have recently been found weighing 238 and 436 lbs. respectively.[2] The total quantity of silver extracted from the Kongsberg mines during 217 years (from 1624 to 1840 inclusive) is 917,557·41 kilog. = 2,023,214 lbs. avoirdupois. The Kongsberg mines were discovered in 1623, and after having been alternately very successful and the reverse, they were abandoned in 1804. In 1815 the working of two of the mines of the district, which were considered to be the most promising, was resumed and continued until 1830, during which period, so far from being productive, they had absorbed large annual subventions from the State to the total amount of about 85,862*l.* In 1830, rich portions having been discovered, it was decided to put up all the mines by auction, with a reserve bidding of 15,000*l.*;

[7] Phil. Mag. 4 ser. 1865. 30. p. 143.
[8] Dana, p. 9.
[9] Ann. d. Mines, 1862. 6. ser. 2. p. 123.
[1] Jameson's Syst. of Mineralogy, 1820. 3. p. 72. Daubrée, Mémoire sur les dépôts métallifères de la Suède et de la Norvége, Ann. des Mines, 1843. 4. ser. 4. p. 259. Durocher, Observations sur les gîtes métallifères de la Suède, de la Norvége et de la Finlande, Ann. des Mines, 1849. 4. ser. 15, p. 351.
[2] Dana's System of Mineralogy, 1868. p. 10.

but there was no offer. The working of these mines was again taken up by the State, and between that date and 1840 yielded a profit of about 461,138*l.* It is stated that native silver constitutes more than four-fifths of the total produce of these mines. In 1750, a mass of native silver, weighing more than 140 lbs., was extracted from Himmelsfürst mine near Freiberg.[3]

Jameson reports (1820) that "Many years ago, a vein of silver was, for a short time, wrought with considerable advantage in the parish of Alva, in the county of Stirling. The metalliferous minerals were native silver and silver-glance, AgS [Ag^2S], with ores of copper and cobalt; and the vein-stones were calcareous-spar and heavy-spar. It is said, that 40,000*l.* to 50,000*l.* worth of silver was extracted from the ores, before the repositories were exhausted. We are told, that a mass of capillary native silver was found in the veins traversing the blue-coloured limestone of the island of Isla."[4]

There is a very rich vein, containing large quantities of native silver, on Silver Islet, north shore of Lake Superior. The native copper from the Minnesota and other Lake Superior mines, United States, contains silver, "sometimes in visible grains, lumps, or strings, and occasionally a mass of copper, when polished, appears sprinkled with large silver spots, resembling a porphyry with its feldspar crystals."[5] A considerable part of the silver in the great Comstock lode in Nevada is in the metallic state.

Native silver in masses exceeding 444 lbs. in weight, is said to have been found at Batopilas, in New Biscay, Mexico. Humboldt notices the occurrence in some parts of Mexico of ochrey-brown iron-ore (gozzan ?), containing minutely disseminated native silver. It is named *pacos* in Peru, and, according to Klaproth, has the following composition :—

Silver	14·0
Hydrated sesquioxide of iron	71·0
Silica	3·5
Sand, etc.	1·0
Water	8·5
	98·0

In 1758 and 1789 two masses of native silver were discovered in the mines of Coronel and Loysa, in Huantaya, Southern Peru, which weighed 8 and 2 quintals (1 quintal = 101·442 lbs. avoirdupois), respectively.[6]

Silver Amalgam.[7]

The recorded localities of this mineral in Europe are Moschellandsberg in the Palatinate, Rosenau in Hungary, Sala in Sweden,

[3] Jameson's Syst. of Mineral., 3. p. 72, quoted from Hausmann's Reise durch Skandinavien in 1806 und 1807, 2. p. 18.
[4] Op. cit. p. 72.
[5] Dana, p. 15.
[6] Jameson's Syst. 3. p. 75.
[7] B. and Miller, p. 125. Dana, p. 13. Ramm. p. 7. Note sur les Amalgames natifs trouvés au Chili : Domeyko, Ann. des Mines, 1862. 6. ser. 2. p. 123; also 1864. 5. p. 457.

A mineral in Spain, and Allemont in France: and in South America the principal are the mines of Arqueros in the province of Coquimbo, Chile, between Huasco and Copiapo in the northern Cordilleras of Chile and at the Rosilla mines in the province of Atacama, Bolivia. The following number of proposed species of amalgams is eight, namely:

I	II	III	IV	V	VI	VII	VIII
$Ag^{3}Hg$	$Ag^{2}Hg$	$Ag^{3}Hg$	$Ag^{10}Hg$	$Ag^{7}Hg$	$Ag^{6}Hg$	$Ag^{5}Hg$	$Ag^{4}Hg$
[$Ag^{6}Hg$	$Ag^{4}Hg$	$Ag^{6}Hg$	$Ag^{20}Hg$	$Ag^{14}Hg$	$Ag^{12}Hg$	$Ag^{10}Hg$	$Ag^{8}Hg$]:

but the evidence in support of the existence of several of these species is unsatisfactory. Domeyko is the authority for all the species, except the second, third and eighth in the foregoing list; and in the detailed descriptions which he has published of the methods of preparing the specimens for analysis, no assurance will be found that he succeeded even with respect to the majority, in obtaining really definite compounds. When any of these alleged amalgams occur crystallized, it is always in the cubical system: yet they differ widely from each other in the proportions of their constituents. Professor J. Cooke has shown that when antimony and zinc are melted together in any proportions, within certain limits which may be considerably apart, alloys are produced well crystallized in the same form, and containing the two metals in the same proportions as they were originally mixed: Matthiessen has remarked the same fact in the case of gold-tin alloys, containing from 27·4% to 43% of gold. It seems probable that in like manner silver and mercury may be alloyed together in various proportions, and yet crystallize in the same form.

Arquerite.—The amalgam, named arquerite, from Arqueros, the locality where it was discovered, has the formula $Ag^{2}Hg$ [$Ag^{3}Hg$], assigned to it by Domeyko. Arqueros is a mineral district, 20 leagues north-west of Coquimbo, in Chile. It is found in regular octahedra, in grains and small masses, and dendritic; and, according to Field, generally massive, and sometimes of a pale yellow colour. The crystallized variety, according to Domeyko, consists of 86·5% of silver, and 13·5% of mercury: a fine sample was analysed by Field, and found to contain 86·24% of silver and 13·72% of mercury. Its sp. gr. is 10·8. Heated in a matrass before the blow-pipe, it yields a sublimate of mercury, without boiling or spirting, as is the case with the amalgam of Mexico (Field). It resembles native silver in colour, lustre, and malleability, but is softer. It is the principal ore of the Arqueros mines (Dana). The matrix of arquerite is sulphate of baryta, and it is almost always associated with cobalt, either as sulphide, or as arseniate of cobalt and lime, the delicate pink colour of which latter upon the sulphate of baryta and silver-amalgam gives the mineral a very beautiful appearance (Field). As much as 1,600,000 ounces of silver were obtained from these mines during the fifteen years succeeding the discovery of the ore.[8] Accord-

[8] Communicated to the Author by Mr. Frederick Field, who was for many years engaged at copper-works at Caldera, Chile.

o Field, many years elapsed before mercury was known to be a tituent of this mineral, and "it astonished the mining proprietors tly, that, whereas other 'maquinas' *lost* a certain amount of mer- in amalgamation, there was a *gain* of mercury at that particular e. It never occurred to them that they were working upon a curial ore!"

Two varieties of amalgam, having formulæ approximating to Hg^4 [Ag^3Hg^2] and AgHg [Ag^2Hg], occur together in asso- ion with yellowish-green chlorobromide of silver: the former is very small, bright, crystalline grains, like bismuthic silver, and ucible to tolerably fine powder by trituration; the latter is in ge grains and irregular masses, malleable, without lustre, and thout the least appearance of crystallization. A round mass of the algam, Ag^5Hg^3 [$Ag^{10}Hg^6$], exceeding 20 lbs. in weight, was dis- vered, in 1857, in the Cordilleras, situated between Huasco and opiapó; it was found by Domeyko, on analysis, to consist of 79·4% silver and 20·6% of mercury; it was the only specimen known, nd was taken by the Chilean Government for the national museum; nd what is particularly noteworthy, it is stated to have "the dentical characteristics of virgin silver, the same colour, lustre, and nalleability."

Kongsbergite.—This is the amalgam of the formula $Ag^{18}Hg$ [$Ag^{36}Hg$], for which Pisani is the authority, who has proposed the name of kongsbergite. It occurs crystallized, and contains from 4·74% to 5·06% of mercury. It is found at Kongsberg, in Norway, along with arquerite.[9]

Silver and Bismuth.

Chilenite (*Dana*). Ag^6Bi [idem].—It was discovered by Domeyko in ores from the silver mine of San Antonio del Potrero Grande, near Copiapó.[1] The specimens, which he first examined, were intimately associated with domeykite, Cu^5As [Cu^3As], and native silver; but long afterwards he obtained specimens free from those minerals. The proportions of silver and bismuth which he found in his first and last analyses are as under:—

	I.		II.
Silver	85·6	.....	84·7
Bismuth	14·4	.....	15·3
	100·0		100·0

These are good grounds for accepting this mineral as a distinct ecies. Domeyko states that "it is disseminated in excessively nall particles, which are occasionally grouped into very irregular ins. These particles present no traces of crystallization. When eshly fractured, they have the lustre and colour of native silver;

[9] Compt. rend. 1872. 75. p. 1274.
[1] Ann. des Mines, 1844. 4. ser. 6. p. 165; also 1864. 6. ser. 5. p. 456.

but they soon tarnish, and acquire a yellowish tint." They are malleable. The mineral analysed by Klaproth and named bismuthic silver, from Schapbach, in Baden, appears to have been nothing more than a mixture of bismuthine, BiS^3 [Bi^2S^3], argentite, AgS [Ag^2S], galena, and sulphides of iron and copper.[2] Several specimens of commercial bismuth have been examined in my laboratory, and found to contain silver in notable quantity, as much even as 60 ozs. per ton; and the silver, which was extracted by cupellation, in every instance yielded a visible quantity of gold.

Silver, Lead, and Gold.

Küstelite.—This is a native alloy of silver, gold, and lead, in which the latter much predominates. Its sp. gr. is 11·32–13·10. It is silver-white in colour, but somewhat darker than native silver when in a fresh state. It is quite malleable, and more easily cut with a knife than native silver. It is found in bean-shaped grains in the lode of the Ophir mine, Nevada. It was first described by Breithaupt, and named by him after its discoverer, Küstel, a well-known metallurgical author. It has been chemically examined by Richter, of Freiberg.[3]

Antimonide of Silver.

Dyscrasite. Ag^4Sb [idem] (?), or Ag^3Sb [idem] (?).—According to the first formula it is when pure composed of 78·22% of silver, and 21·78% of antimony. It crystallizes in the prismatic system (Miller). Its sp. gr. was formerly stated to be 9·44–9·82, but these numbers will require correction, if the results of Petersen's examination, stated further on, be accepted as correct. It is opaque; metallic in lustre; silver-white, inclining to tin-white, as does also its streak; sectile; uneven in fracture. It occurs massive and disseminated, as well as crystallized. Its recorded localities are Andreasberg, in the Harz; formerly Altwolfach, in Baden; Allemont (Dauphiné), in France; Guadalcanal, in Spain; Mexico; and Bolivia. An analysis by Klaproth of a specimen of antimonial silver from Wolfach, and an analysis by Plattner of another specimen of it from Andreasberg, point to the formula Ag^6Sb [idem]. Two varieties of antimonial silver occurring in Chile have been examined by Domeyko, of which the composition is indicated by the formulæ Ag^4Sb [idem] and $Ag^{10}Sb$ [idem], respectively.[4] The evidence, however, upon which the existence of all, not excepting even that of the formula Ag^4Sb [idem], is founded, cannot be received as final: the latter was from the lower part of the mine named Rosario; it was found by Domeyko to consist of 94·2% of silver and 5·8% of antimony. The same mineralogist also found native silver from the lower part of the mine named Descubridora to

[2] Fr. Sandberger, Jahresber. 1863. p. 797. On the Chemical Composition of some Chilean Minerals: D. Forbes, Phil. Mag. 1863. 4. ser. 25. p. 105.

[3] Berg- u. hüttenm. Zeit. 1866. 25. p. 169.

[4] D. Forbes, Phil. Mag. 1863. 4. ser. 25. p. 106.

ist of 95·9% of silver and 4·1% of antimony, and that from the named San Antonio, near Copiapó, to consist of 98·1% of silver, of antimony, and 1% of copper. He examined in 1855 a mass of ve silver from the Descubridora mine, near Copiapó, the weight of ch exceeded 1 cwt., and found it to contain 98% of silver, about of antimony, and small quantities of mercury, arsenic, and cobalt. T. Petersen, in a review of the analyses of dyscrasite, tries to w that there are two native compounds of antimony and silver, of which he names *stibiotriargentite*, Ag^6Sb [idem], and the r *stibiohexargentite*, Ag^6Sb [idem]. The sp. gr. of the former ·611—9·77, and that of the latter 10·027. Any analysis, which s not correspond to one of those two formulæ, Petersen con- rs to be erroneous, or to have been made of a mixture of the ve minerals.[5] My friend Professor Josiah Cooke, of Harvard lege, U.S., concludes from his numerous experiments on the ys of silver and antimony, that the formula of dyscrasite should Ag^3Sb [idem], and that this alloy is isomorphous with anti- nide of zinc of the formula Zn^3Sb [Zn^3Sb^2]. He obtained ll crystals of the artificial alloy, prepared according to this mula, which were sufficiently distinct to prove, that both it and native alloy had the same cleavages, and that the angle between cleavage planes, which he could not measure within a degree, s approximately the same in both.[6] This view has received con- nation from an analysis by Rammelsberg of antimonial silver from Gnade Gottes mine at Andreasberg, one portion of which was stallized, had the sp. gr. 9·729, and agreed in composition with the mula Ag^3Sb [idem]. The composition of the other portion, ich had the sp. gr. 9·851, was represented approximately by the mula $Ag^{10}Sb^3$ [idem] or Ag^7Sb^2 [idem].[7]

Arsenide of Silver.

Arsenical silver.—This name has been applied to a mineral from Samson mine at Andreasberg, in the Harz, on the authority of lyses by Klaproth and Du Ménil; but specimens of the mineral n the same locality have been subsequently examined by Ram- sberg, and proved not to deserve the name. The composition, rding to this chemist, is as follows:—

Analysis of Arsenical Silver (so-called).

Silver	8·88	....	8·81	....	8·24
Antimony	15·46	....	..	....	15·43
Arsenic	49·10	....	..	....	..
Iron	24·60	....	21·33	....	..
Sulphur	0·85	....	..	....	1·10
	98·89				

[5] Dana, Appendix by G. J. Brush, p. 5. Quoted from Poggendorff's al. 137. p. 377.

[6] MS. communication to the Author.

[7] Jahresber. 1864. p. 826.

Its sp. gr. was 7·73. The mineral was silver-white, and homogeneous throughout, showing only a little native arsenic and isolated dark particles. Considered as an isomorphous mixture, its composition would be nearly represented by the formula AgFe + AsSb [$Ag^2Fe+2AsSb$]. It may, however, be regarded as a mixture of mispickel, FeS^2 + FeAs [FeS^2 + $FeAs^2$], arsenical pyrites or lölingite, Fe^4As^3 [Fe^3As^2], and antimonial silver, Ag^2Sb^3 [idem].[8]

I received from Mr. Thomas Macfarlane in person (March 1873) a fine specimen of an arsenical silver ore from Silver-Islet mine, Thunder Cape, Lake Superior. It has a metallic lustre, and is dark grey. It is intermixed with metallic silver, and here and there upon the specimen are light green spots, which doubtless owe their colour to copper. The matrix is calc-spar. The mineral, according to Mr. Macfarlane, was found by blowpipe assay to have the following composition per cent.:—

Silver	78·34
Arsenic, etc. (by difference)	5·98
Nickel	12·93
Cobalt	2·75
	100·00

The following statement of the produce of this mine, which was communicated to me by Mr. Macfarlane, may be interesting:—

PRODUCE OF SILVER-ISLET MINE.

Year.	Ore, lbs.	Value per ton of 2000 lbs.	Total value in gold currency.
1869	27,073⅓	$1646·80	$23.115·35
1870	155,543	1175·80	92,153·23
1871	183,453	1507·64	138,291·88
*	778,468½	1296·48	504,640·13
*	10,000	1040·00	5,200·00
	1,154,537½	$1322·44	$763,400·59

* It is presumed that these quantities refer to other classes of ore raised in the year 1871.

Forbes has examined several specimens from Copiapó, there named arsenide of silver, which he found to be merely mechanical mixtures of native arsenic and native silver. A specimen from Punta Brava, near Copiapó, was "native arsenic, massive, but curiously woven through with wonderfully fine filaments or threads of native silver free from arsenic." Domeyko has described a mineral from Bandurias, varying in colour from lead-grey to tin-white, and occurring in a matrix of argillaceous carbonate of lime. By trituration and levigation the ore was resolved into three metallic substances, namely, flattened malleable metallic grains (I.), heavy metallic powder (II.),

[8] Ramm. p. 28.

and a lighter black earth-like powder (III.). The composition of these substances was found to be respectively as under :—

	I.	II.	III.
Silver	82·5	39·8	1·50
Arsenic	10·1	27·1	53·70
Antimony	0·8	1·0	..
Iron	0·3	13·8	1·90
Cobalt	0·6	8·3	11·55
Nickel	..	0·6	3·75
Mercury	5·6	..	..
Sulphur	..	..	0·15
Vein-stuff	..	8·2	26·50
	99·9	98·8	99·05

Forbes computes that the composition of these substances may be represented by the following formulæ : [9]—

I. Ag^6As [idem] or $(AgHgFeCo)^6As$ $[(Ag^2HgFeCo)^3As]$.
II. $(AgFeCo)^3As$ $[Ag^3FeCo)^3As^2]$.
III. It is regarded as argentiferous smaltine, CoAs $[CoAs^2]$.

My friend Mr. Field informs me that an analysis by him of a mineral from Chile gave the following composition per cent. :—

Silver	12·56
Arsenic	79·21
Cobalt	3·24
	95·01

In repeated analyses of this mineral there occurred the same loss of about 5%, which he discovered was owing to the presence of a large quantity of arsenious acid, which dissolved out on digestion with water : the true composition of this mineral was as under :—

Silver	12·56
Arsenic, metallic	66·17
Arsenious acid	17·22
Cobalt	3·24
Oxide of cobalt	traces
	99·19

On examining this mineral under a powerful lens, the silver was seen to be in the *metallic* state in very minute crystals, "dusted over the mass of partially oxidized arsenic." (Communicated to the Author in 1869. The mineral had been obtained from Chile about 12 years previously.)

Antimonio-Arsenide of Silver.

At Chañarcillo, near Copiapó, a mineral, having a metallic lustre and resembling native silver, occurs disseminated in grains through

[9] Phil. Mag. 1863. 4. ser. 25. p. 107.

carbonate of lime, which may be separated by acetic acid. prepared, its composition was found by Domeyko to be as und

	I.		II.
Silver	53·6	.....	53·3
Iron	3·0	.....	3·0
Arsenic	23·8	.....	22·3
Antimony	19·6	.....	21·4
	100·0		100·0

Domeyko considers the iron to exist as biarsenide, and the re to be represented by the formula

$$Ag^2Sb^3 + Ag^2As^3 \text{ or } Ag^2 (SbAs)^3 \text{ [idem]}.$$[1]

Dana proposes the name of chanarcillite for this mineral.[2]

Sulphide of Silver.

Argentite. Vitreous Silver. Silberglanz, Glaserz (German) [Ag^2S].—When pure it contains 87·097% of silver and 12·9 sulphur. It crystallizes in the cubical system. Sp. gr. = 7·19 (Dana). It is opaque; metallic in lustre; blackish lead-gre shining streak; somewhat malleable and flexible; uneven in f It is the ore from which silver is very largely derived, parti in Mexico. It is found in the deeper part of most silver m Chile, particularly in Tres Puntas and in the neighbourh Huasco, very often crystallized in cubes, octahedra, and dode (Field). A compact variety from Joachimsthal has been fo Lindaker to be composed as follows:[3]—

Sulphide of silver	89·07
Sulphide of lead	4·25
Bisulphide of iron	4·32
Disulphide of copper	1·91
	99·55

Sulphide of Silver and Copper.

Stromeyerite (Brooke and Miller, Dana), Silberkupferglanz (G $AgS + Cu^2S$ [$Ag^2S + Cu^2S$].—It crystallizes in the prismatic (Miller). Sp. gr. = 6·25. It is opaque; metallic in lustre; t lead-grey, with shining streak; sectile. It is isomorphou vitreous copper ore or redruthite, Cu^2S [idem]. When pu composed of 53·1% of silver, 31·1% of copper, and 15·8% of s It occurs crystallized at Rudelstadt, in Silesia, and amorp Schlangenberg, in Siberia, and in Peru. According to Dome cupriferous silver ores of Chile mostly consist of this miner variable proportions of vitreous copper ore intimately inte

[1] Phil. Mag. 1863. 4. ser. 25. p. 107.
[2] Dana, p. 36.
[3] Ramm. p. 52.
[4] Description et Analyses de espèces minérales trouvées au C meyko, Ann. d. Mines, 1843, 4. s

The mines, reported to have yielded such ores in considerable quantity, are those of Catemo, in the province of Aconcagua, and of San Pedro Nolasco, in the province of Santiago. The double sulphides of silver and copper of Catemo are described as amorphous, iron-grey, a little bluish, fine-grained, uneven in fracture, tender, easily sectile, polishable by burnishing, and somewhat malleable. They are not very homogeneous; for in their interior may be perceived dull, nearly compact parts, mixed with bright, granular, occasionally sub-lamellar parts. The vein-stuff is feldspathic; and the only associated mineral is galena, with occasionally black oxide, carbonate, and silicate of copper. The vein-stuff is so intimately mixed with the mineral, that it was not possible to separate perfectly pure pieces of it for analysis.

These double sulphides are auriferous. The ores of San Pedro Nolasco differ from those of Catemo only in structure, which is sub-lamellar, and is due to the structure of the mineral and the mode of its distribution in the matrix: the mineral is in excessively thin, curved, and very irregular plates. The matrix is pearl spar, sulphate of baryta, and ochreous clay. The mineral is never met with either pure or crystallized, and is always associated with galena and blende. Domeyko's analyses are recorded in the following table, with the addition of others of recent date by Taylor and Collier:—

	I. San Pedro.	II. Catemo.	III. Catemo.	IV. Catemo.	V. San Pedro.	VI. Copiapo.	VII. Arizona.	VIII. Arizona.
Silver	2·96	12·08	16·58	24·04	28·79	69·59	14·05	7·42
Copper ...	75·51	63·98	60·58	53·94	53·38	11·12	64·02	72·73
Iron	0·74	2·53	2·31	2·09	..	2·86	0·48	0·33
Mercury .	..	..	..	..	..	..	1·30	..
Sulphur .	20·79	21·41	20·53	19·95*	17·83	16·35	19·44	19·41
	100·00	100·00	100·00	100·02	100·00	99·92	99·29	99·89

* Doubtless a typographical error: it should be 19·93.

Nos. I.—V., by Domeyko; estimating the iron as FeS^2 [idem], Rammelsberg has deduced the following formulæ,[5]—II. = $AgS + 9Cu^2S$ [$Ag^2S + 9Cu^2S$]; III. = $AgS + 6Cu^2S$ [$Ag^2S + 6Cu^2S$]; IV. = $AgS + 4Cu^2S$ [$Ag^2S + 4Cu^2S$]; V. = $AgS + 3Cu^2S$ [$Ag^2S + 3Cu^2S$]. No. VI., by W. J. Taylor (1859), from the Heintzelman mine; it corresponds to the formula $(AgCu^2Fe)S$ [$Ag^2Cu^2Fe)S$].[6] Nos. VII., VIII., by P. Collier.

In Arizona, at the Cerro Colorado mine, stromeyerite is found associated with fahlerz (tetrahedrite), blende, galena, and native silver: the matrix is quartz, with some sulphate of baryta (barytes), and carbonates of magnesia and lime. This class of ore constitutes about 10% of the total ore raised; and the average yield of silver, calculated on the whole quantity of ore smelted, is nearly $1000 to the ton of 2000 lbs., or about 15% of silver.[7]

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[5] Ramm. p. 53. [6] Dana, p. 54. [7] Pumpelly, Mineralogical Sketch of the Silver Mines of Arizona, read before the California Academy of Natural Sciences, Aug. 5, 1861, vol. 2, 1862, quoted from Mowry's treatise, entitled "Arizona

Jalpaite. $3AgS+Cu^2S$ [$3Ag^2S+Cu^2S$].—This formula is deduced from the following analysis by R. Richter, professor at Leoben :—

			Calculated from the above formula.
Silver	71·51	.....	71·76
Copper	13·12	.....	14·06
Iron	0·79	.....	..
Sulphur	14·36	.....	14·18
	99·78		100·00

It crystallizes in the cubical system. Its sp. gr. is 6·877–6·890. It is metallic in lustre; blackish blue-grey; malleable. Its only recorded locality is Jalpa, in Mexico.[8]

Sulphide of Silver, Bismuth, and Lead.

Schirmerite[1] *(Genth).* $2(AgS+BiS^3)+PbS$ [$2(Ag^2S+Bi^2S^3)+PbS$]. —It was discovered by Genth; the locality is not stated.

The results of Genth's analyses, after deducting a small quantity of quartz in each case, are as follow :—

	I.		II.
Silver	22·82	.....	24·75
Bismuth	46·91	.....	47·27
Lead	12·69	.....	12·76
Zinc	0·08	.....	0·13
Iron	0·03	.....	0·07
Sulphur	14·41	.....	15·02
	96·94		100·00

Genth states that it is massive and finely granular, soft yet brittle. Its fracture is uneven, and no cleavage could be observed. Its lustre is metallic, and its colour lead-grey inclining to iron-black: its sp. gr. is 6·737. It occurs disseminated through quartz. It is allied to, and closely resembles, cosalite, a mineral having the formula $2PbS + BiS$ [$2PbS + Bi^2S^3$], and containing 2% or 3% of silver.[2]

Sulphide of Silver and Iron.

Sternbergite.—The following formulæ have been proposed for it: —$AgS + 2Fe^2S^3$ [$Ag^2S + 2Fe^2S^3$];[3] $3AgS,Fe^2S^3 + 2(3FeS,Fe^2S^3)$, or

and Sonora, the Geography, History, and Resources of the Silver Region of North America," New York, 1864. 3rd ed. p. 163.

[8] A. Breithaupt, Berg- u. hüttenm. Zeitung, 1858. p. 85; Ramm. p. 54.

[1] Endlich has given this name to a telluride of silver and other metals from Colorado, which Genth states is "evidently nothing else but a mixture of petzite, either with pyrites or perhaps with a telluride of iron—a mineral which has not yet been found in its *pure* state, the existence of which, however, is probable from the fact that both the true and the auriferous hessites [see p. 211], which are quite *free* from sulphur, invariably contain a minute quantity of iron—which according to my analyses varies from 0·15 to 1·35 per cent."

[2] Proc. of the Amer. Philos. Soc. of Philadelphia. 1874. 14. p. 230.

[3] B. and Miller, p. 179.

$3(\frac{1}{3}AgS,\frac{2}{3}FeS) + Fe^2S^3$ [$3Ag^2S,Fe^2S^3 + 2(3FeS,Fe^2S^3)$];[4] $AgS + 3FeS + FeS^2$, or $4(\frac{1}{4}Ag\frac{3}{4}Fe)S + FeS^2$ [$Ag^2S + 3FeS + FeS^2$].[5] An analysis, by Zippe, of the mineral from Joachimsthal, in Bohemia, gave the following composition per cent.:—

Silver	33·2
Iron	36·0
Sulphur	30·0
	99·2

It crystallizes in the prismatic system (Miller). Its sp. gr. is 4·215. It is metallic in lustre; its colour is usually described as pinchbeck-brown, that is, of a variety of brass, named after Mr. Pinchbeck,[6] of London, which, probably, not one mineralogical writer ever saw; its streak is black, and, like plumbago, it marks paper; it is easily sectile, and, in thin leaves, flexible. It occurs in attached crystals, in fan-shaped and globular aggregations, and in columnar masses; and is found in veins, along with argentite, stephanite, and pyrargyrite, at Joachimsthal, in Bohemia, and at Schneeberg and Johann-Georgenstadt, in Saxony.[7]

Sulphide of Silver, Copper, Zinc, Lead, and Iron.

Castillite.—Its composition, according to the analysis of Rammelsberg, is as follows:—

Silver	4·64
Copper	41·11
Zinc	12·09
Lead	10·04
Iron	6·49
Sulphur	25·65
	100·02

The formula suggested by Rammelsberg is $(Cu^2Ag)S + 2(CuPbZnFe)S$ [$(CuAg)^2S + 2(CuPbZnFe)S$]. Its sp. gr. is 5·186–5·241. It is described as massive; distinctly foliated; metallic in lustre; having the colour and tarnish of purple copper ore or bornite, $3Cu^2S + Fe^2S^3$ [idem]. Its locality is Guanasevi, in Mexico, where it was regarded as argentiferous bornite.[8]

Sulphide of Silver and Antimony.

Polyargyrite. Weichglaserz (Germ.). $12AgS + SbS^3$ [$12Ag^2S + Sb^2S^3$]. —This mineral was discovered at Wolfach in Baden, and described

[4] Ramm. p. 120. [5] Dana, p. 54.

[6] Mr. Christopher Pinchbeck was for some years a member of the Smeatonian Society of Civil Engineers, and for more than a year before his death, which occurred in March, 1783, he was president of the society. He kept a toy-shop in Cockspur Street. The alloy which bears his name consists of about 75% of copper and 25% of zinc, and was used for watch-cases and other articles. (See Evans' Catalogue of Engraved Portraits.)

[7] B. and Miller, p. 180; Dana, loc. cit.

[8] Dana, p. 46.

by Petersen in 1869.[9] It crystallizes in the cubical system, and occurs in the form of the cube, octahedron, rhombic dodecahedron, and icositetrahedron. Its sp. gr. is 6·974. Its lustre is metallic, its colour varies from iron-black to dark lead-grey, and it gives a black streak. Petersen found its composition to be as follows:—

Sulphur	14·78
Antimony	6·98
Silver	76·70
Lead	trace
Iron	0·36
Zinc	0·30
	99·12

Stephanite. Brittle sulphide of silver. Sprödglaserz (German).—The formula $6AgS+SbS^3$ [$6Ag^2S+Sb^2S^3$] was formerly accepted, from which the calculated composition is 71·01% of silver, 13·19% of antimony, and 15·80% of sulphur. But Rammelsberg suggests that the formula $5AgS+SbS^3$ [$5Ag^2S+Sb^2S^3$] more nearly agrees with the results of the analysis by H. Rose, of the mineral from Schemnitz, in Hungary, and of that by Kerl, of the mineral from Andreasberg, in the Harz. These results are as under:—

	I.		II.	Calculated from the last-mentioned formula.
Silver	68·54	....	68·38	.... 68·49
Antimony	14·68	....	15·79	.... 15·27
Copper	0·64	....	..	.... ..
Iron	..	....	0·14	.... ..
Sulphur	16·42	....	16·51	.... 16·24
	100·28		100·82	100·00

I. By H. Rose. II. By Kerl. It crystallizes in the prismatic system (Miller). The sp. gr. of the mineral from Przibram has been found to be 6·269. It is opaque, except when very thin; metallic in lustre; what is called iron-black in colour, as is also its streak; sectile; and conchoidal or uneven in fracture. It occurs in tabular and short columnar crystals, massive, disseminated, coating other minerals, and globular, with a drusy surface (Brooke and Miller). Its recorded localities are Freiberg, Schneeberg, Johann-Georgenstadt, in Saxony; Andreasberg, in the Harz; Joachimsthal, Przibram, Ratieborzitz, in Bohemia; Schemnitz, Kremnitz, in Hungary; Zacatecas, and other places in Mexico; and Peru.[1]

Fire-blende. Pyrostilpnite (Dana).—It has been found to contain 62·3% of silver, and before the blowpipe to give the reactions of sulphur and antimony. It crystallizes in the oblique system (Miller). Its sp. gr. is 4·2–4·3. It is described as translucent, hyacinth-red,

[9] Poggendorff's Annalen, 1869. 137. p. 386.

[1] B. and Miller, p. 98; Dana, p. 106; Ramm. p. 99.

pearly in lustre, inclining to adamantine; sectile, and somewhat flexible. It occurs in delicate crystals. Its recorded localities are Andreasberg, in the Harz; Przibram, in Bohemia; and the Kurprinz mine, near Freiberg.[2]

Pyrargyrite. Dark red silver ore. Dunkles Rothgültigerz (German). $3AgS+SbS^3$ [$3Ag^2S+Sb^2S^3$].—When pure it is composed of 59·95% of silver, 22·28% of antimony, and 17·77% of sulphur. It crystallizes in the rhombohedral system (Miller). Its sp. gr. is 5·75–5·85. It is opaque or translucent; adamantine in lustre; what is termed cochineal-red, more or less red, or blackish lead-grey, as is also its streak; slightly sectile; and conchoidal in fracture. It decrepitates when heated. It occurs massive, as well as crystallized. Its recorded localities are Andreasberg, in the Harz; Freiberg, in Saxony; Joachimsthal, Altwoschitz and Ratieborzitz, in Bohemia; Wolfach, in Baden; Schemnitz and Kremnitz, in Hungary; Norway; Guadalcanal, in Spain; Callington, in Cornwall; Guanaxuato and Zacatecas, in Mexico; Washoe, Austin, in Nevada; and near Copiapó, in Chile. At Poormanlode, Idaho, it has been found in masses of several hundredweights, associated with chloride of silver.[3]

Miargyrite. $AgS+SbS^2$ [$Ag^2S+Sb^2S^3$].—When pure it is composed of 36·95% of silver, 41·16% of antimony, and 21·89% of sulphur. The formula is deduced from the following analysis by H. Rose of the mineral from Bräunsdorf:—

Silver	36·40
Antimony	39·14
Copper	1·06
Iron	0·62
Sulphur	21·95
	99·17

It crystallizes in the oblique system (Miller). Its sp. gr. is 5·3–5·4. It is blackish lead-grey, inclining to iron-black and steel-grey, with cherry-red streak; opaque, but in thin splinters transmitting blood-red light; adamantine in lustre, inclining to metallic; very sectile; somewhat conchoidal in fracture. It decrepitates when heated. It is found at Bräunsdorf, near Freiberg, in Saxony.[4] There are also two supposed varieties of this mineral, named kenngottite and hypargyrite, which have not been completely investigated.[5]

Sulphide of Silver and Arsenic.

Proustite. Light red silver ore. Lichtes Rothgültigerz (German). $3AgS+AsS^3$ [$3Ag^2S+As^2S^3$].—When pure, it is composed of 65·41% of silver, 15·19% of arsenic, and 19·40% of sulphur. It crystallizes in the rhombohedral system (Miller). Its sp. gr. is 5·42–5·56. It is cochineal-red, as is also its streak; semi-trans-

[2] B. and Miller, p. 216; Dana, p. 93.
[3] B. and Miller, p. 211; Dana, p. 94; Ramm. p. 84.
[4] B. and Miller, p. 214; Ramm. p. 81.
[5] Dana, p. 88.

parent; adamantine in lustre; slightly sectile; conchoidal or uneven in fracture. It decrepitates when heated. It occurs massive, botryoidal, disseminated, and coating other minerals, as well as crystallized. Its recorded localities are Schneeberg, Johann-Georgenstadt, Annaberg, Marienberg, and Freiberg, in Saxony; Joachimsthal, in Bohemia; Wolfach, in Baden; Markirchen (Alsace), and Chalanches (Dauphiné), in France; Guadalcanal, in Spain; Mexico; Nevada; and near Copiapó, in Chile.[6] A specimen from Joachimsthal, analysed by H. Rose, contained 0·69% of antimony.

Xanthocone. $3AgS,AsS^{5}$ + $2(3AgS,AsS^{3})$ [$3Ag^{3}S,As^{3}S^{5}$ + $2(3Ag^{3}S,As^{3}S^{5})$].—This formula is deduced from the two following analyses by Plattner, of the mineral from the Himmelsfürst mine, near Freiberg, in Saxony.

	I.		II.		Calculated from the above formula.
Silver	64·18	....	63·88	....	64·05
Arsenic	13·49	....	14·32	....	14·86
Iron	0·97	....	..	....	..
Sulphur	21·36	....	21·80	....	21·09
	100·00		100·00		100·00

It crystallizes in the rhombohedral system (Miller). Its sp. gr. is 5·158–5·191. It is described as transparent or translucent; adamantine in lustre; from orange-yellow to brown in colour, as is also its streak, but darker; brittle; conchoidal or uneven in fracture. It derives its name from the yellow colour of its powder. It occurs in extremely thin crystals, and in small reniform concretions. Its only recorded locality is that above mentioned.[7]

Sulphide of Silver, Copper, Antimony, and Arsenic.

Polybasite. $9(AgCu^{2})S + (SbAs)S^{3}$ [$9(AgCu)^{2}S + (SbAs)^{2}S^{5}$].—This formula is deduced from the following analyses of the mineral from six different localities:—

	I. Schemnitz.	II. Freiberg.	III. Przibram.	IV. Cornwall.	V. Guarisamey, Mexico.	VI. Tres Puntas, Chile.
Silver	72·43	69·99	68·55	72·01	64·29	64·3
Antimony	0·25	8·39	11·53	5·46	5·09	4·2
Arsenic	6·23	1·17	..	3·41	3·74	4·1
Copper	3·04	4·11	3·36	3·36	9·93	9·0
Iron	0·33	0·29	0·14	0·34	0·06	0·7
Zinc	0·59	..	..	..	..	..
Sulphur	16·83	16·35	15·55	15·87	17·04	16·1
	99·70	100·30	99·13	100·45	100·15	98·4

[6] See the same authorities as referred to in the description of pyrargyrite.
[7] B. and Miller, p. 216; Ramm. p. 85.

Nos. I., II., V., by H. Rose. No. III. by Tonner. No. IV. by Joy. No. VI. by Domeyko: the specimen analysed contained 1·6% of matrix. The sp. gr. of this mineral is 6·082–6·218. It crystallizes in the prismatic system (Miller). It is described as opaque, except in thin crystals, when it transmits light of cherry-red colour; metallic in lustre; iron-black, as is also its streak; sectile; uneven in fracture. It occurs in thin tabular crystals, massive, and disseminated. Its recorded localities are those above mentioned, and Guanaxuato and Guadalupe y Calvo, in Mexico; the Comstock Lode and the Reese River mines, in Nevada; and the Owyhee district, in Idaho.[8]

Sulphide of Silver, Antimony, and Lead.

Brongniardite. $AgS + PbS + SbS^3$ [$Ag^2S + PbS + Sb^2S^3$].—Its sp. gr. is 5·95. It is metallic in lustre, like that of bournonite; uneven in fracture, without cleavage. Three analyses of it have been made by Damour, of which the results closely agree; and the mean composition deduced from these analyses is as follows:—

		Ratio of equivalents.	
		Old atomic weights.	New atomic weights.
Silver	24·77	1	2
Lead	24·91	1	1
Antimony	29·77	1	2
Copper	0·62		
Iron	0·26		
Zinc	0·36		
Sulphur	19·24	5	5
	99·93		

The locality of the mineral examined is Mexico. The specimen received by Damour was a compact mass, weighing about 7 kilogrammes, and iron-pyrites was disseminated over one of its surfaces.[9]

Freieslebenite. Schilfglaserz (German).—Several formulæ have been proposed for this mineral, deduced from the following analyses by Wöhler, Escosura, and Payr, of specimens from the Himmelsfürst mine, near Freiberg, from the Santa Cecilia mine at Hiendelencina, in Spain, and from Przibram, in Bohemia, respectively:—

	I. By Wöhler (mean of three analyses).	II. By Escosura.	III. By Payr.
Silver	22·03	22·45	23·08
Lead	30·27	31·90	30·77
Antimony	27·38	26·83	27·11
Copper	1·22	..	..
Iron	0·11	..	0·63
Sulphur	18·74	17·60	18·41
	100·65	98·78	100·00

[8] B. and Miller, p. 209; Dana, p. 107; Ramm. p. 101.

[9] Notice sur la Brongniardite, nouvelle Espèce minérale: A. Damour, Ann. des Mines, 1849. 4. ser. 16. p. 227.

According to Rammelsberg the composition is indicated by the formula $9RS + 4SbS^3$ [$9RS + 4Sb^2S^5$], which may be represented thus:—$3RS,2SbS^3 + 2(3RS,SbS^5)$, or $3(2RS.SbS^3) + 3RS,SbS^5$ [$3(2RS,Sb^2S^5) + 3RS,Sb^2S^5$]. Dana proposes the formula $5(PbAg)S + 2SbS^3$ [$5(PbAg^2)S + 2Sb^2S^3$], and Brooke and Miller propose the formula $RS,SbS^3 + 2(3RS,SbS^3)$ [$RS,SbS^3S^3 + 2(3RS,Sb^2S^3)$]. It crystallizes in the oblique system (Miller). The sp. gr. of No. I. = 6·194; of No. II. = 5·6–5·7; of No. III. = 6·23. It is opaque; metallic in lustre; steel-grey, as is also its streak; sectile, but rather brittle; uneven in fracture. It occurs in crystals, massive, and disseminated. Its recorded localities are those above stated, Kapnik, in Transylvania (a variety containing bismuth); Ratieborzitz, in Bohemia; and Felsobanya, in Hungary.[1]

Sulphide of Silver, Antimony, Copper, and Iron.

Stylotypite. $3(Cu^2AgFe)S + SbS^3$ [$3(Cu^2Ag^2Fe)S + Sb^2S^3$].—This formula rests upon the following analysis by Von Kobell:—

Silver	8·30
Antimony	30·53
Copper	28·00
Iron	7·00
Sulphur	24·30
	98·13

It crystallizes in the prismatic system (Miller). Its sp. gr. is 4·79. It is described as metallic in lustre; iron-black, as is also its streak; sub-conchoidal; uneven in fracture. Its locality is Copiapó, Chile.[2]

Fahlerz. Grey copper ore. Tetrahedrite.—There are three classes of this mineral, namely (I.) antimonio-sulphides, (II.) arsenio-sulphides, and (III.) antimonio-arsenio-sulphides. They form a group of isomorphous mixtures of sulphur-salts, in which the sulphur of the base and acid is in the ratio 4 : 3. The assumed individual component salts may be represented as follow:—

(I.) $4Cu^2S + SbS^3$; $4AgS + SbS^3$; $4HgS + SbS^3$; $4ZnS + SbS^3$; $4FeS + SbS^3$.
[$4Cu^2S + Sb^2S^3$; $4Ag^2S + Sb^2S^3$; $4HgS + Sb^2S^3$; $4ZnS + Sb^2S^3$; $4FeS + Sb^2S^3$.]
(II.) $4Cu^2S + AsS^3$; $4AgS + AsS^3$; $4HgS + AsS^3$; $4ZnS + AsS^3$; $4FeS + AsS^3$.
[$4Cu^2S + As^2S^3$; $4Ag^2S + As^2S^3$; $4HgS + As^2S^3$; $4ZnS + As^2S^3$; $4FeS + As^2S^3$.]

The general formula may be thus expressed: $4RS + (SbAs)S^3$ [$4RS + (SbAs)^2S^3$]. In fifteen analyses of fahlerz belonging to No. I., tabulated by Rammelsberg, silver ranges from 31·29% to 0·25%, antimony from 28·78% to 22%, copper from 37·95% to 14·81%, iron from 7·00% to 2·24%, zinc from 5·77% to 0·00%, sulphur from 28·00% to 21·17%. In ten analyses of fahlerz belonging to No. II., tabulated by Rammelsberg, silver does not appear amongst the constituents, but it is incidentally stated that in three instances it was present: in the first

[1] B. and Miller, p. 208; Dana, p. 93; Ramm. p. 82; Ann. des Mines, 1855. 5. ser. 8. p. 495, quoted from the Revista minéra, 6. p 358.

[2] Dana, p. 98.

to the amount of 0·5% (from Trezavean, Cornwall), in the second 0·4%, and in the third only a trace,—sulphur from 30·25% to 10%. In twelve analyses of fahlerz belonging to No. III., and *not containing mercury*, tabulated by Rammelsberg, silver is not mentioned in three of them, and in the others it ranges from 10·53% to 0·30%, but in only one of these does it exceed 2·37%, antimony from 25·65% to 12·4%, arsenic from 11·55% to 0·75%, copper from 41·57% to 30·73%, iron from 13·50% to 0·86%, zinc from 7·29% to 0·00%, and sulphur from 27·25% to 18·50%. In eleven analyses of fahlerz belonging to No. III., and *containing mercury*, tabulated by Rammelsberg, silver is not mentioned in four, and in the others it ranges from 0·33% to 0·07%, mercury from 17·27% to 0·52%, antimony from 33·30% to 19·34%, arsenic appears only in two and ranges from 4·23% to 2·94%, copper from 39·04% to 30·58%, iron from 9·46% to 0·87%, zinc is only mentioned in five and ranges from 6·24% to 0·69%, sulphur from 26% to 19·38%. From the variation in composition, it is to be expected there would be considerable differences in the external characters of many of the minerals designated fahlerz. It crystallizes in the cubical system: many of the simple forms are hemihedral with inclined faces. The sp. gr. is stated to be 4·5–5·2. It is opaque; metallic in lustre; from steel-grey to iron-black in colour; from black to dark-red in streak; conchoidal or uneven in fracture; somewhat brittle.[3] Fahlerz is found in numerous localities, of which the chief of such as are notably argentiferous are Clausthal, Meiseberg near Neudorf, in the Harz; Freiberg, in Saxony; near Wolfach, in Baden; Kremnitz, in Hungary; Cabarrus county, in North Carolina; Arizona: and Nevada.[4]

In February 1867 I received from my friend Mr. Thomas a sample of richly argentiferous fahlerz from the Foxdale mines, in the Isle of Man, which in the same month was assayed in my laboratory, and found to contain 9·218% of silver (=3011 oz. 4 dwt. 6 grs. per ton) and 24·81% of copper. In August of the same year I received another sample from Mr. Thomas, which was found to contain 4·44% of silver (=1450 oz. 8 dwt. per ton); and in May 1869 I received a third sample from the same source, which was found to contain 4·10% of silver (=1339 oz. 6 dwt. 16 grs. per ton). The assays were made by R. Smith. At the end of 1867 Forbes published the following analysis of this mineral:[5]—

Silver	13·57
Copper	22·62
Zinc	4·65
Iron	4·80
Lead	1·43
Antimony	24·85
Sulphur	27·48
Quartz	0·34
	99·74

[3] B. and Miller, p. 205; Dana, p. 100. [4] Ramm. p. 85; Dana, p. 100.
[5] Phil. Mag. 1867. 4. ser. 34. p. 350.

The mineral in my possession is massive, and is intermixed with galena and copper-pyrites. It is metallic in lustre; light-grey, of an antimonial tint; finely granular; and uneven in fracture. The sp. gr. of the mineral analysed by Forbes was 4·97.

I am indebted to my friend and former student Mr. W. Ratcliffe, who was for some years engaged as an assayer in Peru, for the following table, showing the proportions of copper, lead, gold, and silver, in the fahlerz and "grey antimony"[6] raised at different Peruvian mines: the samples were assayed as they were raised from the mines, without being dressed or selected in any way; the vein-stuff is stated to have been chiefly quartz:—

TABLE SHOWING THE PROPORTIONS OF COPPER, LEAD, SILVER, AND GOLD IN PERUVIAN ORES.

Name of Ore.	Name of Mint.	Copper per cent.	Lead per cent.	Gold.		Silver.	
				Troy oz. per ton.	Per cent.	Troy oz per ton.	Per cent.
Fahlerz	Huancarama	7·9	...	0·65	0·0019	10	0·0306
„	Yanahuanca	9·6	...	0·98	0·0031	90	0·2755
„	Santa Maria	6·2	...	...	...	177	0·5417
„	Gonzales....	1·2	...	...	...	190	0·5815
„	San Blas....	10·1	1·00	...	...	438	0·3406
„	Asuncion ...	14·5	...	2·22	0·0067	278	0·8508
„	Los Muertos	11·5	...	...	...	212	0·6489
„	La Confianza	7·2	...	...	...	540	1·6530
„	San Domingo	1·9	...	...	...	361	1·1049
„	San Pedro...	8·2	...	...	...	533	1·6316
Grey antimony	Ampanu	...	Sb&Pb% 55·5	1·71	0·0054	1874	5·7365

Weissgültigerz. Polytelite.—The mineral thus named, which is found at the Hoffnung Gottes mine, near Freiberg, is massive; metallic in lustre; light-grey, of antimonial tint; finely granular. It is associated with some iron-pyrites and zinc-blende; yet on fracture it seems pretty homogeneous. Its sp. gr. is 5·438–5·465. An analysis of it by Rammelsberg gave the following composition:[7]—

Silver	5·78
Lead	38·36
Zinc	6·79
Iron	3·83
Copper	0·32
Antimony	22·39
Sulphur	22·53
	100·00

[6] Mr. Ratcliffe has informed me (1876) that by "grey antimony" is meant the common sulphide; *i.e.* stibnite of B. and Miller, and antimonite of Dana; but it is stated to have contained lead.

[7] Ramm. p. 99.

He suggests the general formula $4RS+SbS^3$ [$4RS+Sb^2S^3$], which, for this particular mineral, becomes—

$$2(4FeS,SbS^3) + 3(4ZnS,SbS^3) + 6\{4(\tfrac{7}{8}Pb\tfrac{1}{8}Ag)S,SbS^3\}$$
$$[2(4FeS,Sb^2S^3) + 3(4ZnS,Sb^2S^3) + 6\{4(\tfrac{7}{8}Pb\tfrac{1}{8}Ag^2)S,Sb^2S^3\}],$$

or $4(AgPbZnFe)S + SbS^3$ [$4(Ag^2PbZnFe)S + Sb^2S^3$], in which the ratio—

$$Fe : Zn : Pb + Ag = 2 : 3 : 6 ; \text{ and } Pb : Ag = 7 : 1.^8$$

Two specimens of the *light* and *dark* varieties from Himmelsfürst mine near Freiberg, analysed by Klaproth, contained respectively 22% and 9·41% of silver, but there is no mention of the presence either of zinc or lead.

Selenide of Silver and Lead.

Naumannite. (AgPb)Se [$(Ag^2Pb)Se$].—This formula is deduced from the following analyses of specimens from the same locality. Tilkerode, by G. Rose and Rammelsberg, respectively:—

	I. By G. Rose.	II. By Rammelsberg.
Silver	65·56	11·67
Lead	4·91	60·15
Selenium	29·53	26·52
	100·00	98·34

The sp. gr. of No. I. is 8·00. It crystallizes in the cubical system. It is described as opaque; bright metallic in lustre; iron-black in colour, as is also its streak; malleable. No. II. is described by Rammelsberg as largely foliated. It occurs in thin plates, granular and massive, along with selenide of lead (*Clausthalite*). Del Rio states that another kind of selenide of silver is found at Tasco, in Mexico, crystallized in hexagonal plates.[9]

Selenide of Silver and Copper.

Eukairite. $AgSe + Cu^2Se$ [$Ag^2Se + Cu^2Se$].—This formula is established by the following analyses by Berzelius and Nordenskiöld:—

	I. By Berzelius.	II. By Nordenskiöld (mean of three analyses).	Calculated from the above formula.
Silver	42·73	43·17	43·08
Copper	25·30	24·66	25·31
Selenium	28·54	32·07	31·61
	96·57	99·90	100·00

[8] Dana, p. 104.

[9] Ramm. p. 34; Dana, p 39.

It is described as opaque; crystalline; metallic in lustre; lead-grey, with shining streak; soft and easily sectile. It occurs massive, granular, and in black metallic films, staining the calcite in which it is contained. The specimens, of which the analyses are given above, came from a copper-mine at Skrikerum in Smaland, Sweden, where it was imbedded in calcite in a kind of serpentine rock. Other recorded localities are Aguas Blancas, near Copiapó, in Chile; the mines of Flamenco, near Tres Puntas, in the desert and province of Atacama; province of San Juan, east side of the Andes, in Chile; and the Cacheuta mine in the province of Mendoza, in Chile.[1]

Selenide of Silver, Copper, and Thallium.

Crookesite. $(Cu^2TlAg)Se$ [$(CuTlAg)^2Se$].—It is described as massive, compact, and amorphous; metallic in lustre; lead-grey; brittle. Its sp. gr. is 6·90. It has been analysed by A. E. Nordenskiöld, whose results are as under:—

Copper	46·11	46·55	44·21
Silver	1·44	5·04	5·09
Iron	0·63	0·36	1·28
Thallium	18·55	16·27	16·89
Selenium	33·27	30·86	32·10
	100 00	99·08	99·57

Its recorded locality is Skrikerum.[2] According to A. E. Nordenskiöld the selenide of copper, named berzelianite, Cu^2Se [idem], which is also found at Skrikerum as a black or bluish-black amorphous powder, disseminated through a coarse crystalline calcite and sometimes forming dendritic crusts, contains notable, yet variable, proportions of silver and a small quantity of thallium. The presence of silver, he suggests, may be due to the intermixture of eukairite. When berzelianite is sufficiently massive to be observed, it is reported to be metallic in lustre, silver-white in fracture, but soon tarnishing; its sp. gr. is 6·71.[3]

Telluride of Silver.

Hessite. Telluric Silver. AgTe [Ag^2Te].—When pure, it is composed of 62·73% of silver and of 37·27% of tellurium. This formula is based on the following analyses:—

	I.		II.	III.
	a.	*b.*		
Silver	62·42	62·32	61·55	64·5
Gold	..	..	0·69	..
Tellurium	36·96	36·89	37·76	33·0
Iron	0·24	0·50	..	..
	99·62	99·71	100·00	97·5

[1] Ramm. p. 34; Dana, p. 39; B. and Miller, p. 151.
[2] Dana, p 40. [3] Idem, p. 795.

	IV.	
	a.	*b.*
Silver	59·91	60·19
Gold	0·22	0·20
Tellurium	37·86	38·07
Iron	1·35	1·20
Copper	0·17	0·16
Lead	0·45	0·18
Zinc	trace	trace
	99·96	100·00

No. I. *a* and *b*. By G. Rose, of the mineral from the Savodinskoi ine, near Barnaul, in Siberia. No. II. By Petz, of the mineral from agyag, in Transylvania. No. III. By Rammelsberg, of a very small antity of the mineral from Retzbanya, in Hungary: the results e only given as approximate. No. IV. *a*. and *b*. By Genth, of the ineral from the Red Cloud mine, Colorado. Its sp. gr. is 8·3–8·6: he sp. gr. of that analysed by Genth was 8·178. It is said to rystallize in the prismatic system of Miller (Orthorhombic, Dana). t is metallic in lustre, between lead-grey and steel-grey in colour, as also its streak, malleable, sectile, without distinct cleavage, and in acture even. The characters of the Red Cloud mine mineral are ated by Genth to be as follow: dark iron-grey in colour inclining to lack, granular in structure, uneven in fracture, and sectile; the colour f the powder is dark lead-grey; it contained cavities lined with inute crystals of iron-pyrites and sulphate of baryta.[4] It occurs in anular masses, along with iron-pyrites, copper-pyrites, and blende talcose slate, in the Savodinskoi mine, and in the Stanislaus mine, alaveras county, California.[5]

Auriferous Hessite.—Under this head Genth classes what appear to only varieties of hessite, which contain gold in notable quantity, t in much less quantity than the mineral to be next described, tzite. The following analyses of auriferous hessite by Genth are the mineral from the Red Cloud mine, Colorado:—

	I.	II.	III.
Silver	59·68	59·83	50·56
Gold	3·31	3·34	13·09
Tellurium	37·60	36·74	34·91
Copper	0·05	0·06	0·07
Lead	..	..	0·17
Zinc	..	..	0·15
Iron	0·15	0·21	0·36
Quartz	0·18	0·13	0·70
	100·97	100·31	100·01
Specific gravity	8·789		8·897

[4] Proceedings of the American Philophical Society of Philadelphia, 1874. p. 229. See also Contributions to ineralogy by F. A. Genth: American Journal of Science and Arts, 45. May 1868.

[5] Dana, p. 50; Rammelsberg, p. 15; B. and Miller, p. 136.

According to Genth, the physical differences between hessite
these varieties of it are so slight that it is almost impossible to
tinguish them from each other. They have all an iron-grey col
and often acquire by tarnishing a darker or purplish colour;
their fracture is subconchoidal: the more argentiferous are somew
darker, and the more auriferous lighter and more brittle.

Telluride of Silver and Gold.

Petzite. (AgAu)Te [(AgAu)^{2}Te].—It contains from 40% to 4
of silver, from 18% to 26% of gold, and from 30% to 36% of telluriu
The following analyses of this mineral have been published:—

	I.	II.	III.	IV.	V.	VI.	VI
Silver	46·76	42·14	41·86	40·87	40·60	40·73	40
Gold	18·26	25·63	25·60	24·97	24·80	24·10	24
Tellurium	34·98	32·23	32·68	34·16	35·40?	33·49	32
Copper	..	..	..	..	..	trace	tr
Bismuth	..	..	..	..	..	0·41	.
Lead	trace	..	..	..	..	0·26	.
Zinc	..	..	..	..	..	0·05	0
Iron	trace	..	..	..	..	0·78	1
Sulphur	trace	..	..	..	..	..	.
Quartz	..	..	..	..	..	0·62	0
	100·00	100·00	100·14	100·00	100·80	100·44	100

No. I. By Petz, of the mineral from Nagyag. No. II. By Gent
of the mineral from the Stanislaus mine, California. Nos. III. an
IV. By Genth, of the mineral from the Golden Rule mine, Californi
No. V. By Küstel, of the mineral from the Stanislaus mine. Nos. V
and VII. By Genth, of the mineral from the Red Cloud min
Colorado. Its specific gravity is, according to Petz, 8·72–8·83
according to Genth, 9·01–9·02; and, according to Küstel, 9·0–9·
It is between steel-grey and iron-black in colour, sometimes wit
iridescent tarnish; its streak is iron-black; brittle. Genth's d
scription of auriferous hessite applies also to the petzite from th
Red Cloud mine, where they are the principal minerals in the ore.

Sylvanite. Graphic Tellurium.—The composition of this miner
varies considerably, as will be seen from the following analyses:—

	I.	II.	III.	IV.	V.
Silver	10·00	14·68	7·47	2·78	13·05
Gold	30·00	24·89	27·10	29·62	24·83
Tellurium	60·00	55·39	51·52	49·96	56·31
Lead	..	2·54	8·16	13·82	..
Antimony	..	2·50	5·75	3·83	..
Copper	..	..	..	..	0·23
Zinc	..	..	..	..	0·45
Iron	..	..	..	..	3·28
Selenium	..	..	..	..	trace
Sulphur	..	..	..	..	1·82
	100·00	100·00	100·00	100·01	99·97

No. I. By Klaproth, of the mineral from Offenbanya. Nos. II., III., IV. By Petz, of the mineral from Offenbanya. No. V. By Genth, of the mineral from the Red Cloud mine, Colorado. Its specific gravity varies from 5·7 to 8·3. It crystallizes in the oblique system of Miller (monoclinic, Dana); its lustre is metallic; its colour, and that of its powder, varies from pure steel-grey to silver-white, but sometimes is nearly brass-yellow. It occurs in twin crystals, with a distinct cleavage; also massive and granular. Its fracture is uneven. Genth states that the mineral from the Red Cloud mine occurs massive, with "eminent cleavage in one direction, giving it a plated appearance. It is at this mine associated with iron-pyrites in very small crystals, often so thickly disseminated through the mass, that it is very difficult to obtain pure material for analysis." The other recorded localities of the mineral are Nagyag, in Transylvania; and the Melones and Stanislaus mines, Calaveras county, California.

Calaverite (*Genth*). $AuTe^4$ [$AuTe^2$], with a little silver replacing gold.—It was discovered by Genth in an ore from the Stanislaus mine, Calaveras county, California. The results of his analyses, after deducting a small quantity of quartz in each case, are as follow:—

	I.		II.
Silver	3·52		3·08
Gold	40·70		40·92
Tellurium	55·89		56·00
	100·11		100·00

According to Genth, it occurs massive and crystallized; its colour is bronze-yellow, and that of its powder yellowish-grey. It is brittle and uneven in fracture, which inclines to sub-conchoidal. It is frequently associated with petzite, to which a portion of the silver in the analyses was attributed.[6]

I am indebted to my friend and former student, Mr. Richard Pearce, of Black Hawk, Colorado, for beautiful and instructive specimens of tellurium minerals from that locality: they are chiefly tellurides of gold; and amongst them are two specimens, which Mr. Pearce believes to be sylvanite; there is also a specimen labelled "oxidized telluride ore," in which gold becomes visible on burnishing.

Chloride of Silver.

Horn-silver. Kerate. Cerargyrite. AgCl [idem].—When pure it contains 75·25% of silver and 24·75% of chlorine, and is stated to be colourless when freshly cut (Field): but in a perfectly pure state it is not so common, in Chile at least, as is generally sup-

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[6] Dana, p. 795.

posed; much of the so-called chloride being in reality the chloro-bromide of silver.[7] Horn-silver crystallizes in the cubical system. Its specific gravity is 5·31–5·60. It is usually massive; transparent or only translucent at the edges; wax-like in appearance; from resinous to adamantine in lustre; colourless, or coloured of various tints, pearl-grey, green, violet-blue, and brown, owing to the presence of different foreign matters, or to exposure to light; shining in streak; conchoidal or uneven in fracture; without cleavage; malleable and sectile. It occurs crystallized, reniform, encrusting other minerals, massive, and occasionally columnar. Amongst its recorded localities the following may be mentioned: Kongsberg, in Norway; Allemont (Dauphiné), Huelgoat (Bretagne), in France; Huel Mexico and Huel St. Vincent, near Calstock, and Dolcoath mine,[8] in Cornwall; Spain; the Saxon mining districts and the Harz, where it is now very scarce; Schlangenberg near Kolywan, in Siberia; in Nevada, in large quantities in the White Pine District; in Idaho and Arizona; Catorce and Zacatecas, in Mexico; Tres Puntas in the province of Atacama, Chañarcillo near Copiapó, and elsewhere in Chile:[9] it is said to be principally found in the mineral district of Chañarcillo, and, in some of the mines, veins of it, more than an inch thick, have been met with two feet below the surface (Field, on the authority of Domeyko).

Chloride of silver and sodium. Huantajaite.—Domeyko has recently published the following account of this mineral, which, he states, has been discovered in Chile by Raymondi of Lima, who has analysed various specimens of it, and found it to consist of 11% of chloride of silver and 89% of chloride of sodium. It crystallizes in cubes; and generally occurs disseminated in small crystalline, diaphanous, brilliant, colourless particles, forming thin crusts upon an argilo-calcareous and slightly ferriferous matrix: it has a saline taste; but its principal character is that of being instantly decomposed by water, with the separation of a white flocculent deposit of chloride of silver. When a stone impregnated with this mineral is moistened, there is formed on the surface a milky substance, which blackens in the light; and hence the miners of Peru designate it *lechedor*, a Spanish word meaning milk-producer.[1] In 1856 I received from my friend Mr. Bollaert, lately deceased, a specimen of a mineral from Huantajaya in Peru, which, he informed me, Domeyko considered to be a compound of chloro-bromide of silver and chloride of sodium, and which was known by the name of *lecheador* (sic). The specimen consists of a piece of grey-coloured rock, which is here and there fissured, and thinly coated, especially in the fissures, with a substance, colourless or nearly so, glassy in lustre, and easily yielding to a pen-knife. In some places in the fissures the substance is distinctly

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[7] Communicated by Mr. Field to the Author.

[8] I have received from my friend and former student, Mr. Pearce, a beautiful specimen of chloride of silver from the Dolcoath mine. Its colour is pale green.

[9] B. and Miller, p. 613; Dana, p. 115.

[1] Ann. des Mines, s. 6. 1876. 10. p. 36.

ystallized; and I detached a particle which, under a lens, appeared ry bright and perfectly colourless, which was brittle, and dissolved the tongue, communicating a saline and decided metallic taste. he substance seems clearly to have been introduced into the spemen through the fissures. I found it to be immediately acted on y water, which dissolved out chloride of sodium and left chloride f silver in the state of white powder. The rocky matrix contains arbonate of lime in large proportion, some carbonate of magnesia, lay, and a little oxide of iron. In one or two places the coating has pale bluish-green colour, indicative of the presence of copper. Information relating to supposed double chlorides of silver and odium has been previously given at pp. 62, 63, of this volume.

Chloride of silver and mercury.—This mineral was discovered by Domeyko, who has published the following description of it:—It differs much in external characters from all the varieties of horn-silver which he had hitherto seen. The colour of its fresh fracture is reddish-brown, yellowish, or hair-brown; but in the course of time, by the action of light, it becomes blackish or nearly black. Its lustre is less bright than that of pure native chloride of silver, and it tarnishes quickly by contact with the air, becoming occasionally semi-metallic. The mineral is less malleable and less compressible than pure native chloride of silver; and the surfaces produced by cutting it with a knife have a certain horny lustre and a honey-yellow colour. It is easily crushed in an agate mortar and reduced to light yellowish powder. When heated in a tube closed at one end, it yields a white sublimate, and, with the addition of carbonate of soda, a sublimate of mercury. From the mean of two analyses of the amorphous mass of this mineral, Domeyko deduced the following composition:—

Silver	66·68	
Mercury	2·20	91·52
Chlorine	22·64	
Chloride of sodium	1·75	
Sesquioxide of iron	1·60	
Silica (insoluble)	1·07	
Carbonate of lime and loss by heat	4·04	
	99·98*	

* In the original paper the sum is given as 100, so that there is probably a typographical error.

This mineral forms small irregular masses in the midst of large masses of ore of chloride of silver, which constitute the riches of the mines of Caracoles, situated between the 23rd and 24th degrees of latitude, in the desert of Atacama, in Bolivia, and regarded actually as the richest mines in South America. The specimen analysed came from the La Julia mine.[2] Large quantities of ore containing chloride

[2] Notice sur divers Minéraux récemment découverts au Chili par M. Ignace Domeyko: Ann. des Mines, s. 6. 1876. 10. p. 15.

of silver, from Caracoles, have been smelted at Swansea, with results in some cases, it is reported, not quite satisfactory.

Chloride of silver, sulphide of silver, and antimonic acid.—The following notice is by Domeyko.[3] He regards this substance, which he designates blue antimoniuretted sulphide of silver (*argent antimonié sulfuré bleu*), as an intimate mixture (or a kind of union) of chloride of silver, sulphide of silver, a small proportion of antimoniuretted silver, and hydrated antimonic acid. In the silver mines of Chile, particularly in those of Lomas Bayas, Copiapó, are found ores very rich in silver, which are always amorphous, and have a bluish colour more or less intense. Sometimes this colour is due to the presence of a small quantity of blue carbonate of copper; but there are ores which contain none of that substance and yet present bluish tints of the same kind. In this case antimoniuretted sulphide and chloride of silver are always found in the ores of silver. Domeyko has received from the La Descubridora mine, of Caracoles, a specimen of the same kind of ore, containing 40% of silver, and sufficiently pure to enable him to ascertain its nature. It is bluish-grey, and in colour resembles certain earthy amorphous blue minerals of phosphate of iron. It is tender, a little compressible, difficult to break, and dull, but acquires a little polish under the knife; it is uniform (*homogène*) in structure, is fine-grained, and passes to an earthy consistence; its fracture is even (*plane*) and irregular (*sic*); and its powder is bluish. When the mineral is treated with weak ammonia-water and afterwards with water, the whole of the chloride of silver dissolves, but the wash-water passes turbid through the filter. On evaporating the wash-water antimonic acid is left, which dissolves with difficulty in strong boiling hydrochloric acid, and is nearly insoluble in a solution of potash. If water acidulated with hydrochloric acid is used for washing instead of pure water, the water becomes still more turbid, and leaves upon the filter a considerable quantity of hydrated antimonic acid, mixed with sulphide of silver. It is impossible to remove by this means all the antimonic acid, even by prolonging the washings and decantations during several days; if rather strong hydrochloric acid is used, it attacks the sulphide of silver, without dissolving the antimonic acid. On account of these difficulties, Domeyko was only able directly to determine the proportion of chloride of silver in the mineral, and the proportions of silver and sulphur in that part of it which was insoluble in ammonia-water, and from which it is easy completely to separate the chloride. Three analyses of different pieces of the mineral yielded the following results:—

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[3] Ann. des Mines, s. 6. 1876. 10. p. 19.

	I.	II.	III.
Chloride of silver	11·3	11·2	10·3
Sulphide of silver	45·2	45·5	50·6
Sulphur in excess, combined with antimony	0·6	1·2	0·9
Antimonic acid and antimony in the antimoniuretted sulphide of silver, which corresponds to the sulphur in excess (by difference)	35·5	34·9	31·2
Loss at an incipient red-heat *	7·2	7·2	7·0
	99·8†	100·0	100·0

* The loss by heat does not certainly represent the water expelled, on account of the partial decomposition which antimonic acid may undergo at the temperature stated. (Note by Domeyko.)
† There is, probably, a typographical error in the decimal column of figures in the analysis.

Domeyko suggests that this mineral probably results from the metamorphosis of black "sulpho-antimoniuretted silver."[4]

Bromide of Silver.[5]

Bromite (*Miller*). *Bromyrite* (*Dana*). *Bromargyrite* (*Rammelsberg*). AgBr [idem].—When pure, it contains 57·45% of silver, and 42·55% of bromine. It crystallizes in the cubical system. Its sp. gr. is 5·8–6·0. The pure mineral is yellow, and is found, according to Field, in large yellow octahedra at only one mine at Chañarcillo, in Chile; has a bright lustre and is sectile. It usually occurs in small crystals. It is the chief constituent of the "Plata Verde" (Spanish), or green-silver ore, of the district of Plateros, and at the San Onofre mine, near Zacatecas, in Mexico; and it occurs in association with chloride of silver at Huelgoat (Bretagne). It was first recognized in Chañarcillo in 1851 by Domeyko; and Field observed that a specimen sent to him from the Delirio mine as iodide of silver was much darker in colour, and proved, on analysis, to be pure bromide.

Chloro-bromide of silver. Embolite. Ag(ClBr) [idem].—This mineral consists of isomorphous mixtures of chloride and bromide of silver in variable proportions, such as are indicated by these formulæ: (I.) 2AgCl + AgBr [idem]; (II.) 3AgCl + 2AgBr [idem]; (III.) AgCl + 3AgBr [idem]. The composition per cent. found by analysis and deduced from these formulæ is as follows:[6]—

	I.		II.		III.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
Silver	68·22	68·22	66·94	66·98	61·07	61·06
Chlorine	14·92	14·93	13·18	13·18	5·00	5.01
Bromine	16·84	16·85	19·82	19·84	33·82	33·93
	99·98	100·00	99·94	100·00	99·89	100·00

[4] Ann. des Mines, s. 6. 1876. 10. p. 19.
[5] If the names bromargyrite and iodargyrite be adopted for bromide and iodide of silver, surely chlorargyrite should be adopted for the chloride. Nothing can be more barbaric than many mineralogical names; but these are preferable to a nomenclature recently proposed with a view to indicate composition. Fahlerz, for example, is designated sulphocuprosoferroussulphantimonite.
[6] Ramm. p. 196.

The analyses are by Field, and the specimens analysed were all from Chañarcillo. The mineral crystallizes in the cubical system. Its sp. gr. is 5·79–5·81. It is resinous or adamantine in lustre; green of varying shades; hackly in fracture; malleable; sectile. It is only partially and with difficulty dissolved by ammonia-water, and is much more fusible and volatile than the chloride of silver (Field). It occurs masssive, stalactitic or concretionary at the surface. It is reported to constitute the chief silver ore of the mines of Chañarcillo, and to be found at various other localities in Chile, as also in Mexico and Honduras.

Iodide of Silver.

Iodite (Miller). Iodyrite (Dana). Iodargyrite (Rammelsberg). AgI [idem]. —When pure, it contains 45·97% of silver, and 54·03% of iodine. It crystallizes in the rhombohedral system of Miller (hexagonal, Dana).[7] Its sp. gr. is 5·50–5·71. It occurs crystalline, massive, and in thin plates. It is resinous, inclining to adamantine in lustre; translucent; sulphur-yellow, yellowish-green or brownish; yellow in streak; flexible when in plates; sectile; fragile and easily reduced to powder (Damour).[8] Its chief recorded localities are Albarradon near Mazapil (Zacatecas), in Mexico; Algodones near Coquimbo, Delirio mines of Chañarcillo, in Chile; Peru; Guadalajara, in Spain; Cerro Colorado mine, in Arizona.

Mr. Field informs me that he has never found a chloro-iodide or bromo-iodide of silver, but that Domeyko states that he *has* detected the presence of iodine in the bromide.

Chloro-iodide of silver, with sulphide of silver, sulphide of lead, and carbonate of lead.—This mixture of minerals has been analysed and described by Domeyko under the name of *sulpho-iodide of silver* (*negrillo* being the Spanish name). It forms an amorphous mass, which is black, inclining somewhat to a bluish tint, tender, porous, occasionally spongy, and always enveloped in a harder, yellowish, ochreous crust. The black mass is not homogeneous: there may be observed some parts richer in horn-silver, which are compressible, and others less rich in silver, which are more easily reduced to powder and effervesce with acids: in contact with the crust, some plates of galena may also be detected. From various incomplete analyses of the black mass, Domeyko has obtained the following results per cent.:—

Iodine	3·57	forming	Iodide of silver	6·61
Chlorine	1·58		Chloride of silver	6·32
Silver	40·47		Sulphide of silver	37·56
Sulphur	6·45		Sulphide of lead	12·15
Oxide of lead				
Carbonate of lead				33·06
Carbonate of lime				—

[7] On the authority of Des Cloizeaux, Compt. rend., Feb. 25, 1867, v. 64.

[8] Damour. Note sur l'Argent iodé du Chili: Ann. des Mines, s. 5. 1853. 4. p. 329.

The enveloping crust, which is ordinarily very heterogeneous, contains neither silver nor iodine, and is in great part composed of carbonate and oxychloride of lead, mixed with insoluble matter. This mineral is from Caracoles, in the mines of which it is not rare, though it is rarer than the chloride of silver and mercury, from the same locality and previously described, and has not been hitherto found by Domeyko in any other silver mine in Chile.[9]

Iodide of Silver and Mercury.

Tocornalite (*Domeyko*). — The formula assigned to it by this mineralogist is $AgI + Hg^2I$ [$2AgI + Hg^2I^2$]. The mineral analysed by him had the following composition per cent. :—

Silver	33·80
Mercury	3·90
Iodine	41·77
Siliceous residue	16·65
	96·12

The loss in this analysis is stated to be due to water and some iodine. It is amorphous or granular in structure, soft, pale-yellow, but darkens on exposure to air, becoming first greyish-green in colour and finally black: it produces a yellow streak. It is found at Chañarcillo.[1]

Chloro-iodide of silver and mercury.—Domeyko has recently examined and described this mineral, which came from the mines of Caracoles, which, he says, still continue to yield annually more than half a million of marcs of silver. It is amorphous, yellow, in colour resembling tocornalite; it blackens rapidly by the action of light; its structure is granular, passing into compact; its fracture is even (*plane*) or uneven; and when scraped, it is pale yellow. It is easily triturated in an agate mortar, and may be reduced to impalpable powder. It is with difficulty, and very imperfectly, reduced by zinc and acidulated water; but it is easily decomposed by sulphuretted hydrogen (*hydrosulfate*), and it was this reagent which Domeyko used in the following incomplete analysis of the mineral :—

	Per cent.
Mercury	18·0
Silver	14·8
Iodine	9·3
Chlorine	4 7

The residue consisted of insoluble matrix, which contained sulphate of baryta and a small proportion of sulphate of lead.

Domeyko was informed that this mineral is occasionally met with in considerable quantity in the mines of Caracoles; but up to the

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[9] Op. cit. p. 16.

[1] Domeyko, 2nd Append. Min. Chili, 1867. p. 41. Note by J. G. Brush to the Author.

present time (1876) it had not been recognized (*on l'a confondu*), and had been sent to the amalgamation works along with other ordinary ores of chloride of silver.[2]

Since the preceding article on Ores of Silver was in type, the following notices of newly-discovered argentiferous minerals have been published.

Polyarsenide of Copper, Silver, and Bismuth.

This new mineral has also been recently described by Domeyko in the following terms:—It is amorphous; its fresh fracture is metallic-grey inclining slightly to yellow, very feeble in lustre, granular in structure, very fine in grain and homogeneous; it tarnishes in the air, becoming blackish and covered with iridescent tints like those of certain varieties of arsenide of copper and of copper-pyrites. On rubbing it with a pen-knife, it acquires a bright silvery lustre, which is permanent. It breaks into fragments with sharp angles and edges; but it offers a certain resistance to crushing by the blow of a hammer or in an agate mortar; its fracture is even or slightly conchoidal; it scratches calc-spar, its hardness being = 3·5; its sp. gr. is from 6·66 to 6·81. It fuses very readily before the blow-pipe, and on melting evolves in the air white arsenical fumes. It is easily attacked by cold nitric acid, yielding a blue solution, which becomes turbid on dilution by water, and in which a copious precipitate is formed on the addition of a drop of hydrochloric acid. On heating this mineral with weak hydrochloric acid, about 10% of protoxide of copper (cupric oxide) is dissolved, along with traces of arsenious acid; and the residue, which is black and unattackable, contains all the arsenide and insoluble siliceous matrix. The composition of the mineral is variable on account of the variable proportion of siliceous matrix and oxide of copper with which it is interpenetrated. The analysis by Domeyko of a perfectly homogeneous fragment yielded the following results:—

Protoxide of copper (cupric oxide)	10·02
Copper	41·86
Silver	28·98
Bismuth	6·91
Arsenic	6·70
Matrix	5·01
	99·48

The mineral came from the mine of San Antonio del Potrero Grande, in the province of Copiapó, and it was in the same mine that thirty years ago Domeyko discovered the native alloy of silver and bismuth (*chilenite*, see p. 193 antea).[3]

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[2] Ann. des Mines, s. 6. 1876. 10. p. 31.

[3] Idem, p. 21.

Mercurial Selenitic Sulphide of Silver.

Under the name of *sulfure d'argent mercuriel séléniteux*, Domeyko has described a substance from the La Descubridora mine in Caracoles, which he states to be more abundant than that previously mentioned, to which he has given the name of sulpho-iodide of silver. It is black, brilliant, and has the three distinct cleavages of selenite, though it cannot, like it, be separated into thin leaves, and is harder than selenite. The selenitic part of the substance may be dissolved out without difficulty by distilled water: by the action of water on the pure mineral, namely, that which has perfect cleavages, there remains about a third of its weight of residue, which contains nearly 2% of mercury and 3% or 4% of antimony. When this residue is treated with pure nitric acid, more than $\frac{9}{10}$ths of its weight of sulphide of silver are dissolved, and there remains a compound of silver, mercury, sulphur, and antimony, upon which nitric acid has scarcely any action. Domeyko found a selected portion of this mineral to consist of 68·89% (by difference) of hydrated sulphate of lime and 31·11% of sulphuretted metals of the following composition:—

Soluble in nitric acid	Sulphide of silver	25·62
Nearly unattackable by nitric acid	Silver	2·77
	Mercury	0·61
	Antimony	1·10
	Sulphur	0·96
		31·06

It occurs in kidney-shaped or irregular masses; it occupies more particularly the internal parts, and is surrounded by ore rich in chloride of silver mixed with hydrated foliated sulphate of lime.[4]

Fahlerz or Grey Copper Ore very rich in Silver.

The following notice of this ore, which occurs at Huanchaca, in Bolivia, has been published by Domeyko. It contains from 12% to 13% of silver, and constitutes the rich part of the very abundant ores from the mines of Huanchaca, of which the half of the property has recently (1876) been purchased for three millions of piastres (about 625,000*l.*). The mineral has quite the same external characters as the highly argentiferous grey copper ore of Oruro and of various other antimonial grey-copper ores poor in silver, or only containing 1% or 2% of that metal, from Peru and Chile. It is generally amorphous, steel-grey in colour, granular in structure, and uneven in fracture; it is rarely crystallized, but little tetrahedrons of it may occasionally be found concealed in the cavities of the amorphous mass. It is associated with galena, sulphide of antimony, pyrites and blende, which contain very small proportions of silver.[5]

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[4] Ann. des Mines. s. 6. 1876. 10. p. 17.

[5] Idem, p. 24.

Other Minerals containing Silver.

The ores of silver previously described are such as constitute mineral species, and contain silver either as an essential or as an isomorphous element. But there are many other ores which contain a compound of silver as an accidental constituent mechanically intermixed. Some native metals also, besides those already mentioned, occur in alloy with silver, and the most striking example is native gold, which is uniformly argentiferous, as will hereafter be shown. We have found both silver and gold in native arsenic from Borneo. Galena is always argentiferous, though in very variable degree, and from that ore of lead a large quantity of silver is annually extracted in the United Kingdom, and other parts of the world. Blende, and sulphuretted ores of copper, sulphuretted and arsenical ores of iron, are occasionally argentiferous.[6] Many examples have been given in the descriptions of lead-smelting processes in the volume on the Metallurgy of Lead by the Author. It was recorded in the volume on Iron and Steel by the Author that silver to the extent of about ½ oz. per ton has been found in a black-band ironstone of South Wales. Malaguti and Durocher assert that they have detected silver in sea-water to the amount of 1 centigramme in a cubic metre; and, assuming the total quantity of sea-water to be two millions of cubic myriamètres and the proportion of silver to be uniform throughout, they compute the total quantity of silver in sea-water to be two millions of tonnes (nearly the same as the English ton), or more than two thousand times the quantity yearly (1850) extracted (?) from the surface of the earth (*fabriquée chaque année à la surface de la terre*).[7]

Note on the Designation of Silver Ores in South America.

I am indebted to my friend Mr. Field for the following information:—The Chilean and Peruvian miners have a singular manner of classifying silver ores which is puzzling to the stranger, who constantly hears of "metales calidos" and "metales frios;" *i.e.*, in Spanish, hot and cold metals. By "metales calidos" is meant all minerals comprising native silver, amalgams, chloride, chloro-bromide, and iodide of silver,—all, in fact, which are suitable for direct amalgamation; and by "metales frios" is meant those which cannot be thus directly treated by amalgamation, but require the accessory processes of calcination, or of treatment with sulphate of copper, chloride of sodium, etc. The former were supposed to be already *hot*, and the latter to need *heat*, either from chemical action or from fire, before the silver could be extracted. Thus, when an ore is very difficult to treat or "beneficiar," as it is termed in Spanish, it is said

[6] Malaguti and Durocher examined a large number of such ores from various localities, and determined the proportions of silver which they contained. See their "Recherches sur l'Association de l'Argent aux Minéraux métalliques," 1850. p. 94.

[7] Op. cit. p. 94.

to be "muy frio," or very cold. The Chilean process of amalgamation will be fully described in the sequel; but here it may be stated that formerly the residues of this process were thrown away. These residues or "relaves," which at first were mud-like, became dry, and were then kneaded with water and built up into the walls of a town, or were thrown upon the sandy soil in order to fit it for the growth of vegetables. In after years, from 1853 to 1858, when the railway from Copiapó to the coast was established, the "relaves" became valuable; the walls were pulled down and the whole town searched thoroughly for "relaves," which were found to yield from 20 to 30 marks (1 mark = 3408 grains troy) of silver per "cajon,"[8] or, in round numbers, from 50 to 70 oz. of silver per ton English, and which were eagerly purchased for exportation to Europe. But, as the cost of carriage from the interior to the coast exceeded the value of the silver of the "relaves," it was necessary to obtain the silver in a concentrated form by smelting it with copper-pyrites, by which means an argentiferous regulus was produced, containing from 300 to 400 ozs. of silver per ton, and from 40% to 50% of copper. This regulus was chiefly sent to Swansea. In thus smelting the "relaves," there was always great loss, owing to the fine argentiferous powder — the "relaves," it must be borne in mind, were originally finely-ground mud—being mechanically carried up the chimney to an "alarming extent," when the contents of the furnace, which was reverberatory, were rabbled, a loss which it was very difficult to prevent.

As every metallurgist cannot be expected to remember the crystallographic nomenclatures of Miller and Dana, and as both are used in the preceding article on Silver Ores, the following table is inserted in order to save the reader the trouble of referring to mineralogical treatises for information on that subject.

CRYSTALLOGRAPHIC NOMENCLATURE OF MILLER AND DANA.

Systems of Miller.	Systems of Dana.
I. Cubical	Monometric.
II. Pyramidal	Dimetric.
III. Rhombohedral.....	Hexagonal.
IV. Prismatic	Trimetric.
V. Oblique	Monoclinic.
VI. Anorthic	Triclinic.

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[8] In Chile the cajon or caxon is equal to 64 quintals or 6400 pounds.

SILVER-ASSAYING.

By this expression is meant the art of ascertaining the quantity of silver in any substance, natural or artificial, which contains that metal; and he, therefore, who practises that art is designated a silver-assayer. The subjects of silver-assaying may be thus classified:—

I. Natural substances, which include not only all the mineral species in which silver is an essential constituent, but all ores containing silver in accidental association or intermixture, whether in the metallic state, or combined, or in both states. Although, strictly speaking, the term silver ore should, perhaps, be restricted to the former, yet it is conventionally extended to the latter when they are sufficiently argentiferous to yield silver with profit by metallurgical treatment. There are, however, ores, *e.g.* certain varieties of pyritic copper ore, from which both copper and silver can be advantageously extracted, and which, therefore, might equally be regarded as copper ores and silver ores. Such ores might be designated argentiferous copper ores, or cupriferous silver ores, according as the copper or the silver is relatively the most valuable constituent.

Further:—In the preceding volume by the Author on the Metallurgy of Lead, which is in great measure introductory to this volume, it has been stated, that though all galena is argentiferous, yet it is only when it contains silver in such quantity as to admit of its profitable extraction, that the adjective argentiferous is applied to it by metallurgists.

II. Artificial substances of various kinds, such as sulphides (*e.g.* argentiferous copper- or iron-regulus),—arsenides (*e.g.* nickel speise),—litharge, old test-bottoms, slags, furnace residua, and old crucibles in which silver or its alloys have been melted,—alloys, and the sweepings of silversmiths' workshops, technically termed "sweep."

The silver in all argentiferous substances, whether natural or artificial, is, except in the case of certain alloys, invariably determined by assaying in the *dry* way, either by direct cupellation with lead, or by previously separating and dissolving the silver in molten lead, and then cupelling the lead. Thus, the substances with which the silver-assayer has to deal are divided into two classes, namely, one of substances which may be directly cupelled, and the other of substances which require treatment preliminary to cupellation. This is an important practical distinction.

The preliminary treatment consists of one or two methods, namely, fusion in a crucible with lead or with substances from which, by the addition of reducing agents and suitable fluxes, lead is separated during the process; and the method of scorification, or roasting in conjunction with lead. These methods, in each of which an alloy of silver and lead is obtained fitted for direct cupellation, will be accordingly designated the fusion method, and the scorification method or simply scorification, respectively.

The following description of silver-assaying consists of two parts, the first relating to the assaying of ores, various furnace products, and "sweep;" and the second relating to the assaying of bullion, coin, and plate. With certain exceptions, the first part has been written by my assistant Mr. R. Smith, who has been engaged in teaching the students of the Royal School of Mines the art of assaying ever since the foundation of the school in 1851, and the second part by Mr. W. Chandler Roberts, F.R.S., formerly a student of the school, and now chemist to the Royal Mint. The second part also comprises the art of gold-assaying, exclusive of the assaying of auriferous ores. It may be objected that this course is unsystematic; and there is, no doubt, some force in the objection. But nevertheless I have, after careful consideration, decided to adopt it, as I find it to be as impossible to treat of the metallurgy of silver without reference to gold, as I found it also to be to treat of the metallurgy of lead without reference to silver.

FIRST PART OF SILVER-ASSAYING.

(ASSAY OF ARGENTIFEROUS ORES, AND METALLURGICAL PRODUCTS.)

It is not proposed to present in this First Part of Silver-Assaying a history of that art, however interesting the subject may be; or to describe all the variations in the methods of assaying, which have been or may still be practised either at home or abroad; but to describe, as concisely as may be compatible with clearness, the art as practised in the Metallurgical Laboratory of the Royal School of Mines.

FURNACES AND IMPLEMENTS.

FURNACES.—Two kinds of furnaces are used,—air-furnaces and muffle-furnaces.

Air-furnace.—The furnace described in a former volume by the Author, containing an article on the Assaying of Copper Ores, is equally suitable for the assaying of silver ores by the *fusion* method. The furnace is represented in the annexed woodcut, fig. 1. *a*, fire-place; *b*, ash-pit; *c*, flue; *d*, main flue, which communicates with a chimney 60 ft. high, and is common to several furnaces; *f*, register; *g*, fire-bar; *h*, *i*, fire-brick covers, each of which is clamped with a piece of flat bar-iron, firmly wedged at

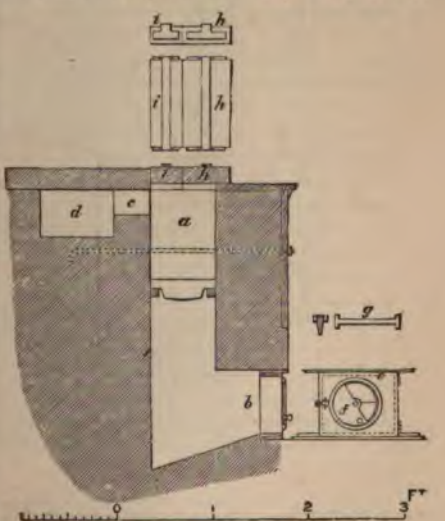


Fig. 1. Air-furnace for assaying. The chamber, *a*, is square in horizontal section.

one end. Coke should be the fuel; but when not obtainable, cha coal may be used.

Muffle furnace.—This furnace is used for the assaying of silver ore by the *scorification* method, and for cupellation. Where a large numbe of assays have to be made by scorification, the muffle-furnace is con structed to receive a muffle capable of holding from 30 to 50 scorifiers in other cases the dimensions shown in the annexed woodcuts figs. 2–7, which are taken from drawings of a muffle-furnace in the Metallurgical Laboratory of the Royal School of Mines, are more suitable. All muffle-furnaces should, as shown in the woodcuts, b provided with dampers and ash-pit registers. The fuel used is coke anthracite, or a mixture of the two.

A form of muffle-furnace in use at Swansea is shown in figs 8–10. The muffle is heated by flame, and the fuel used is bituminou coal.

MUFFLES.—These are vessels in which cupels or scorifiers ar heated, so that the substances operated upon may be protected fro

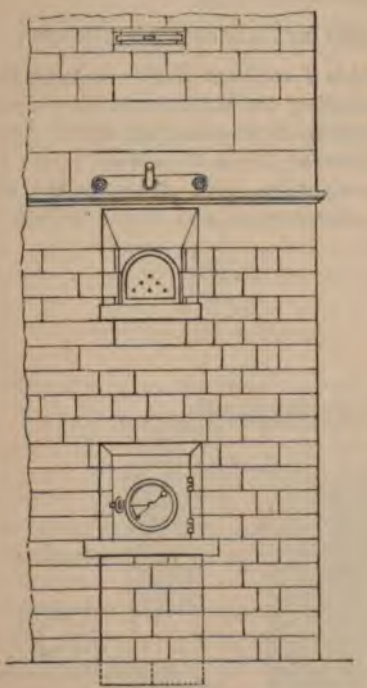
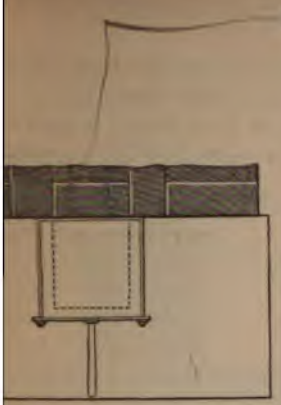


Fig. 2. Muffle-furnace. Front elevation. In this and figs. 3 and 4, the muffle, which is an open-mouthed D-shaped vessel of fire-clay, is shown in its normal position, with the flat side or bottom downwards. In front it rests upon the fire-brick supported by the fire-bars. It should may enter except through the mouth itself.

Fig. 3. Muffle-furnace. Vertical section throu the middle of the furnace, at right angles the axis of the muffle.

front wall of the furnace, and at the back o be clayed well round the mouth, so that no



Muffle-furnace. Plan of the top, showing the cover on.

Fig. 6. Iron key for lifting the muffle-door.

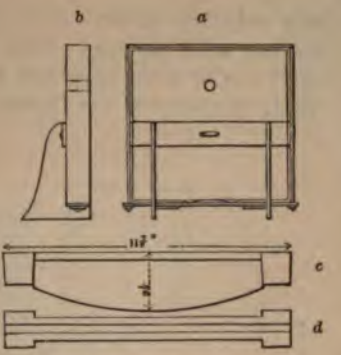


Fig. 7. *a*, Muffle-door; *b*, do. and elevation. The door consists of a single fire-brick, set in a framework of wrought-iron; there is a hole through as shown in *a*, by means of which air may be admitted and the interior of the muffle inspected. Firebar; *d*, do. in plan, from which it will be seen that a shallow groove extends from end to end.

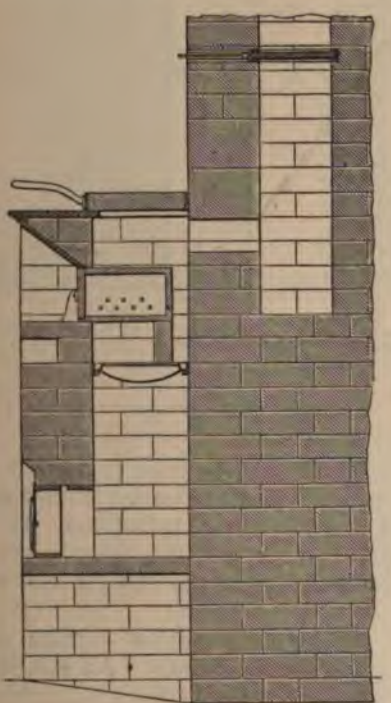


Fig. 4. Muffle-furnace. Vertical section through the middle of the furnace and the axis of the muffle. The holes in the back are not shown in this woodcut.

the reducing action of the gases evolved from the fuel, and contact with particles of the fuel or of its ashes. They are pr with one or more openings in the sides or back, or in both, in that, by means of the furnace draught, a current of air may b

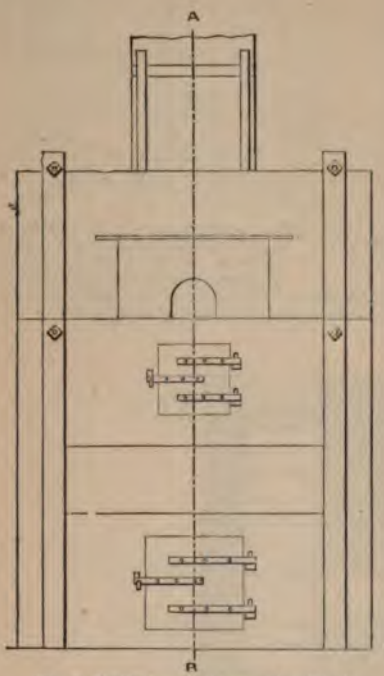


Fig. 8. Muffle-furnace (Swansea). Front elevation.

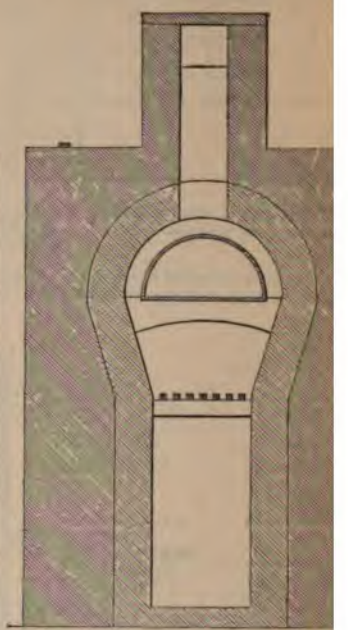
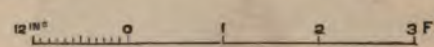


Fig. 9. Muffle-furnace (Swansea). Sec on line C, D, fig. 10.



constantly passing through them, from around the door at the r and through a hole in the door itself. Muffles are generally of fire-clay, and are kiln-burnt before use. It is necessary the position, number, and size of the holes in the muffle shou carefully adjusted according to the draught of the furnace and circumstances.

Crucibles.—Two kinds of crucibles—earthen and wrought-i are used; but generally the former. An article on the subj crucibles will be found in the Author's volume on Fuel, etc. lished 1875).

Earthen crucibles.—The varieties designated Cornish, Lo Hessian, and French are suitable. Cornish crucibles of the siz shape indicated in fig. 11 will be found generally serviceable.

Wrought-iron crucibles.—They are made of various shapes and but are always circular in horizontal section: in some work

med ones are used. Crucibles of the form and dimensions shown
. 12 are generally suitable.

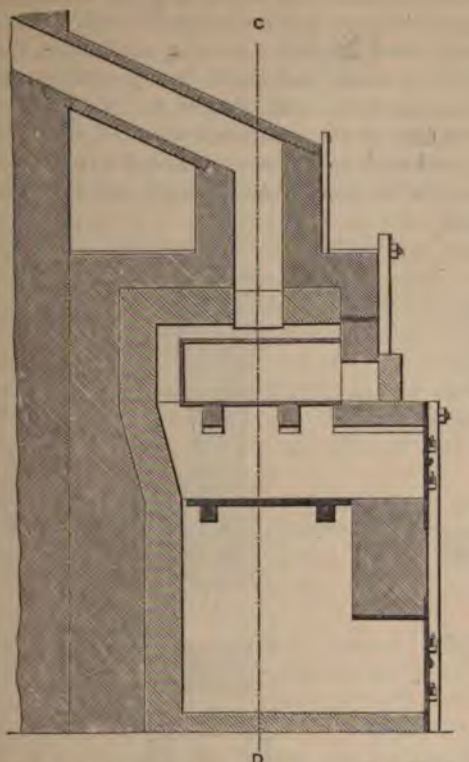
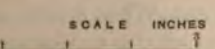


Fig. 10. Muffle-furnace (Swansea). Section on line A, B, fig. 8. In figs. 9 and 10 the lighter sectional shading represents fire-brick.

Fig. 11. Cornish crucible.

Fig. 12. Wrought-iron crucible.



Scorifiers.—Scorifiers are shallow, circular, cup-shaped vessels, le of fire-clay, in which the substances to be subjected to scori-

fication are placed. They are made of various sizes; but that of the form and dimensions shown at B, fig. 13, is recommended.

A scorifier should resist as much as possible the corrosive action, at high temperatures, of molten oxide of lead, either by itself or in admixture with other highly corrosive substances, such as oxide of copper or iron. It should not crack on exposure to great and sudden changes of temperature. It should be wide across the top, so that a large surface of the materials operated upon may be exposed to oxidation; and so deep in the centre that a considerable proportion of the lead used in the process may be kept well covered and preserved from oxidation.

Fig. 13. Scorifier (B), with mould (C) and plug (A), shown in vertical section through the centre.
Scale = ¼th.

Fig. 14. Cupel (B), with mould (C) and plug (A), shown in vertical section through the centre. The cavity of the mould and the lower part of the plug taper slightly downwards, and are not cylindrical, as here shown.
Scale = ¼th.

Fig. 15. Cupel (B), with mould (C) and plug (A), shown in vertical section through the centre.
Scale = ¼th.

Good scorifiers cannot always be readily obtained. Those manufactured for sale are often badly shaped and very liable to crack when heated, and are easily and irregularly corroded by oxide of lead. The scorifiers manufactured by Morgan Brothers, of Battersea, and by Howell, of Swansea, have been used in the Metallurgical Laboratory of the Royal School of Mines, and have given satisfaction, especially the latter.

Manufacture of scorifiers.—When scorifiers are used in large numbers they are frequently made at the smelting-works. A mixture of two parts by measure of raw, and one part of burnt, Stourbridge clay may be employed; the following mixture has also been found to answer

well, viz., equal parts by measure of best Stourbridge fire-clay, best Stourbridge fire-bricks ground to powder, and that variety of kaolin which is sold under the name of pipe-clay. The materials should not be in too fine a state of division, as in that case the scorifiers would be too close in grain, and therefore too liable to crack on heating.

Scorifiers may be formed by hand in a metal mould, by means of a plug, much in the same way as the small crucibles described by the Author, in a volume on Fuel and Refractory Materials, published in 1875. The plug, A, and mould, C, are shown in fig. 13. A sufficient quantity of the mixture, after having been carefully kneaded with water to the proper degree of plasticity, is put into the mould, previously smeared internally with oil; the plug, also oiled, is driven home by a few blows with a wooden mallet, turned round once or twice, and then removed. The scorifier is carefully pushed out of the mould from below, dried, and afterwards fired at such a temperature as to give it a cream colour, when it is ready for use. If the temperature has not been sufficiently high, the scorifier will be tender; and if too high, it will have a brownish tint, and be too liable to crack when heated. They are always sold in the kiln-burnt state.

Roasting Dishes.—Roasting dishes are flat, shallow, circular vessels of fire-clay. They are sometimes employed for the roasting of regulus, and of ores containing sulphides or arsenides, an operation which may be conducted in a muffle, or by placing the roasting dish in front of the flue of an air-furnace.

Cupels.—In old treatises on assaying these articles were termed "coppels." Both cupel and coppel are derived from the French word "coupelle," which means a little vessel in the form of a cup.

Cupels are small vessels, generally in the form of an inverted truncated cone, as shown at B, fig. 15, and having the upper surface fashioned into a shallow concavity. They are made of bone-ash, and vary in size, according to requirements: those upon which buttons of 250, 500, and 1000 grains of lead, respectively, can be cupelled are most generally useful. A cupel of the usual form is represented at B, fig. 14. A cupel should be capable of absorbing its own weight of molten litharge: this will serve as a guide in the selection of cupels of suitable size. The mode of preparing bone-ash is described in the sequel at p. 237.

Manufacture of cupels.—The process is conducted as follows:—Finely-ground bone-ash is moistened with water and thoroughly kneaded, so that the mass may be of uniform consistence throughout, and quite free from lumps. The material is of the proper consistence when it coheres by gently squeezing it in the hand. If too much water has been used, the cupel will be too dense and compact; if too little, it will be tender and friable.

The apparatus used for making cupels consists of two parts, the mould and the plug or plunger, which are named in French and German "the nun" and "the monk," respectively. Both parts may be made of iron, brass, or gun-metal.

The plug, A, and mould, C, of the form usually employed, are represented in fig. 14. In forming the cupel, a thin disk of metal is first dropped into the cavity and falls to the bottom of the mould. A quantity of bone-ash, prepared as above described, and varying with the desired thickness of the cupel, is then put into the mould; and the plug is driven down by a wooden mallet, turned round once or twice, and afterwards withdrawn. The cupel is then carefully pushed out through the top of the mould, by pressing the fingers against the disk at the bottom; it should afterwards be well air-dried, and heated just before being used for about 15 minutes, to expel all traces of moisture.

Cupels are also made in such a mould as is shown at B, fig. 15; it consists of two parts, the outer one being intended solely to keep the plug perfectly central.

When a very large number of cupels are required, a press may be conveniently used. Greater rapidity of manufacture may thus be obtained, as well as greater uniformity in the size and substance of the cupels.

The cupels which Chaudet most frequently used weighed, on the average, from 12 to 14 grammes, and were capable of absorbing about their own weight of lead; they were 17 millimetres high and 24 millimetres in diameter at their base, and 30 millimetres at the top; the diameter of the cavity at the top was 26 millimetres, and the depth 7 millimetres, and the thickness of the bottom 10 millimetres.[1]

Cupel-Trays.—Trays for holding cupels are generally made of sheet-iron, with or without partitions. Two different forms are shown in figs. 16A and 16B.

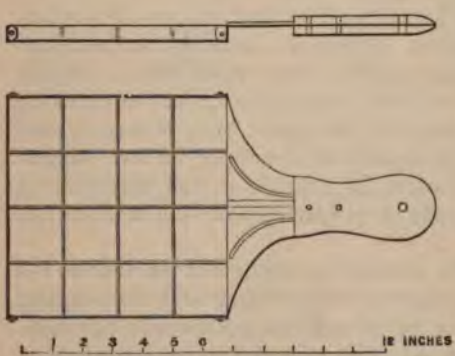


Fig. 16A. Cupel-tray, with partitions, shown in side elevation and plan.

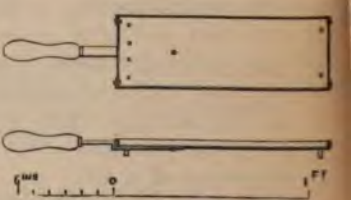


Fig. 16B. Cupel-tray, without partitions, shown in plan and section.

Tongs.—The following different kinds of tongs are used, viz. furnace-tongs, cupellation-tongs, and scorification-tongs.

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[1] L'Art de l'Essayeur, p. 17.

Furnace-tongs.—These are used in assaying in the air-furnace. For earthen crucibles, those shown at C in fig. 17 are suitable: for iron crucibles, heavier ones are better, such as are represented at A and B, fig. 17.

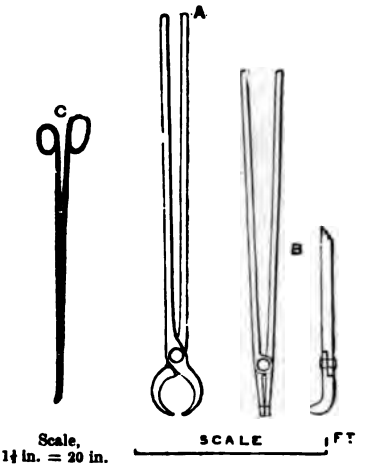

Fig. 17. Furnace-tongs.

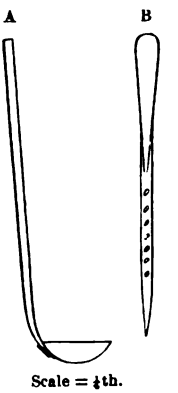

Fig. 18. Ladle (A) and spatula (B).

Cupellation-tongs.—These are used for moving the cupel. They are made of different sizes and relative proportions. The tongs represented at A, fig. 19, will be found generally suitable.

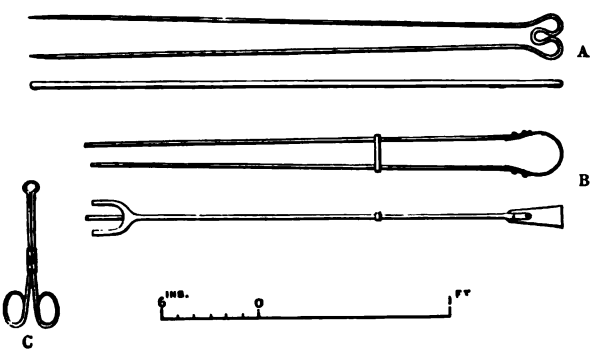

Fig. 19. A, cupellation-tongs, in plan and side elevation.
B, scorification-tongs, in side elevation and plan.
C, tongs for lifting parting-flasks (see p. 261).

Scorification-tongs.—These are used for moving the scorifier. For this purpose the lower leg is divided near the end into two fork-like prongs, the upper leg being made straight throughout. They are of different shapes and sizes: those represented at B, fig. 19, will be found generally suitable.

Scoop.—This is generally made of copper, and is employed chie for charging crucibles; it is shown in fig. 20. It should be k smooth and bright.

Fig. 20. Scoop, shown in plan and side elevation. Scale=$\frac{1}{4}$th.

Measuring Ladle.—This is made of copper, and is used fo measuring the granulated lead. The bowl holds 500 grs. whe filled level at the surface. It is shown at A, fig. 18.

Spatula.—This is made of steel. The blade end is used fo mixing, and the pointed end for breaking down hard lumps i calcining. It is shown at B, fig. 18; the small elliptical marking upon the woodcut are intended to represent notches, by means c which it may be firmly held.

Stirrer.—A round rod of iron about a quarter of an inch i diameter, flattened out at one end, is generally used as a stirrer When required in calcining in a muffle, the flattened-out end is ben at right angles for the distance of about an inch.

Ingot-moulds.—Ingot-moulds are either open or closed, and ar generally made of cast-iron; open moulds have either hemispherical c conical cavities, as shown at C and D, fig. 21. When a large number assays have to be made, a mould of thick sheet-iron, containing 9 c 12 hemispherical cavities, formed by hammering, is sometimes used.

When thin flat ingots are required, a closed mould such as is i common use and may be purchased at hardware shops is necessary it is made of cast-iron in two parts, which are clamped together b a screw, as shown in fig. 22.

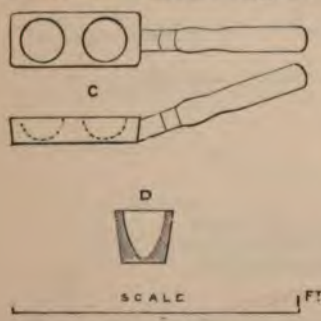

Fig. 21. Ingot-moulds.

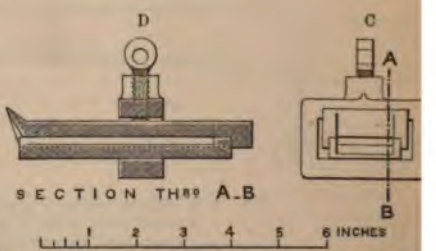

Fig. 22. Mould for casting flat ingots. C, end view of t mouth end. D, section on the line A B. When in u it is fixed vertically or slightly inclined.

Hammers, Forceps, and Brushes.—These should be of variou sizes; and the brushes should have stiff bristles, such as those of nail-brush.

Sieves.—Wire sieves of various sizes and fineness should be at hand.

Balances.—Three are usually employed. One, for weighing fluxes and reagents, which should carry one pound, and turn with half a grain. A second, for weighing out the ore, which should carry 500 grains, and turn with $\frac{1}{200}$ of a grain. A third, for weighing the silver assay-buttons, which should carry 30 grains, and turn with $\frac{1}{1000}$ of a grain; but a balance constructed to carry 500 grains, and to turn with $\frac{1}{1000}$ of a grain, will be found more generally useful.

Weights.—Special weights are used for weighing the assay-buttons—or "prills," as they are technically termed—of silver, to facilitate calculation. These weights vary according to the manner in which the quantity of silver in the ore is returned by the assayer. In England and Australia, the quantity of silver is reported in ounces, pennyweights, and grains (Troy), upon the statute ton of 2240 lbs. (Avoirdupois): in Canada and the United States, it is reported in the number of dollars-worth of silver upon the ton of 2000 lbs. (Avoirdupois).

The following special weights will be found convenient, as they indicate the number of ounces of silver per ton of ore, on the assumption that 100 grains of ore are taken for the assay: when only 50 grains are used, as in scorification, the number of ounces of silver, indicated by the weight, must be multiplied by 2 in order to obtain the true number of ounces per ton of ore:—

Actual weights in grains.	Corresponding number of ounces per ton of ore.
30·61225	10,000
18·36732	6,000
9·18366	3,000
6·12244	2,000
3·06122	1,000
1·83673	600
0·91836	300
0·61224	200
0·30612	100
0·18367	60
0·09183	30
0·06122	20
0·03061	10
0·01836	6
0·00918	3
0·00612	2
0·00306	1

The numbers stated in the first column represent the actual weights deduced by calculation; but it is hardly necessary to remark that the weights produced by the balance-maker cannot be relied on as absolutely accurate beyond the third or fourth decimal.

The weights, with the exception of the rider, are made of platinum: those which represent from 100 to 10,000 ounces per ton are flat and square, and have the weights which they indicate stamped upon them: those which indicate from 1 to 60 ounces per ton are made of wire of two different diameters, bent into a variable number of lengths,

corresponding to the number of ounces per ton which they represe
the form of the weights is shown in fig. 23.

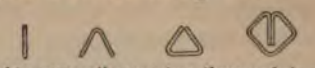

Fig. 23. Weights representing one, two, three, and six ounces per ton.

The balance has a rider, made of gold or aluminium, the weigh
which represents 10 ounces per ton, and its beam is divided i
hundredths; so that the quantity of silver can be returned to $\frac{1}{10}$
an ounce per ton when 100 grains are taken for the assay.

When special weights are not employed, the following table
be found useful:—

TABLE FOR COMPUTING FROM THE PERCENTAGE OF SILVER THE TROY WEIGH
OF SILVER PER STATUTE TON.

Per cent.	Per ton.				Per cent.	Per ton.		
	Grains.	ozs.	dwts.	grs.		Grains.	ozs.	dwts.
0·0001	15·68	0	0	15·68	0·06	9,408·0	19	12
0·0002	31·36	0	1	7·36	0·07	10,976·0	22	17
0·0003	47·04	0	1	23·04	0·08	12,544·0	26	2
0·0004	62·72	0	2	14·72	0·09	14,112·0	29	8
0·0005	78·40	0	3	6·40	0·1	15,680·0	32	13
0·0006	94·08	0	3	22·08	0·2	31,360·0	65	6
0·0007	109·76	0	4	13·76	0·3	47,040·0	98	0
0·0008	125·44	0	5	5·44	0·4	62,720·0	130	13
0·0009	141·12	0	5	21·12	0·5	78,400·0	163	6
0·001	156·8	0	6	12·8	0·6	94,080·0	196	0
0·002	313·6	0	13	1·6	0·7	109,760·0	228	13
0·003	470·4	0	19	14·4	0·8	125,440·0	261	6
0·004	627·2	1	6	3·2	0·9	141,120·0	294	0
0·005	784·0	1	12	16·0	1·0	156,800·0	326	13
0·006	940 8	1	19	4·8	2·0	313,600·0	653	6
0·007	1,097·6	2	5	17·6	3·0	470,400·0	980	0
0·008	1,254·4	2	12	6·4	4·0	627,200·0	1306	13
0·009	1,411·2	2	18	19·2	5·0	784,000·0	1633	6
0·01	1,568·0	3	5	8·0	6·0	940,800·0	1960	0
0·02	3,136·0	6	10	16·0	7·0	1,097,600·0	2286	13
0·03	4,704·0	9	16	0·0	8·0	1,254,400·0	2613	6
0·04	6,272·0	13	1	8·0	9·0	1,411,200·0	2940	0
0·05	7,840·0	16	6	16·0	10·0	1,568,000·0	3266	13

[COMPOSITION OF BONE AND PREPARATION OF BONE-ASH, BY THE AUT

COMPOSITION OF BONE.—The inorganic matter of the bones
mammals may, in general, be regarded as having the follow
composition:[2]—

	Per cent.
Phosphate of lime	57
Carbonate of lime	8
Fluoride of calcium	1
Phosphate of magnesia	1
Cartilage	33
	100

[2] Physiological Chemistry. By Professor C. G. Lehmann. Translated by George E. Day, M.D., F.R.S., and published by the Cavendish Society, 1
3. p. 18.

Thus, the inorganic matter amounts to 67%, and the organic matter to 33%. The formula of the phosphate of lime is $3CaO,PO^5$ [$Ca^3P^2O^8$], and not $8CaO,3PO^5$ [$Ca^5P^6O^{25}$] as Berzelius supposed.[3]

The composition of ox-bones was found by Berzelius to be as follows:[4]—

	Per cent.
Phosphate of lime, with fluoride of calcium	63·15
Carbonate of lime	1·38
Phosphate of magnesia	2·07
Soda, with a little chloride of sodium	2·40
Cartilage and vessels	31·00
	100·00

In the process of analysis followed by Berzelius, it has been shown that a considerable quantity of lime was erroneously estimated as phosphate instead of carbonate.

Cartilaginous matter yields by incineration, with access of air, a residue which is stated to consist of phosphates of lime, magnesia and soda, chloride of sodium, carbonate and sulphate of soda, and sulphate of potash, and ferric oxide; the sulphuric acid of the sulphates being produced by atmospheric oxidation of the sulphur in the cartilage in the presence of the fixed alkalies or their carbonates. Frommherz and Gugert found that 100 parts of cartilage (dried at about 100° C.) of the false ribs of a young man, æt. 20, yielded an ash from which the carbon could not be wholly removed by incineration. By exhausting this ash with water and acids, inorganic matter to the extent of 3·402% of the weight of the cartilage was dissolved, and had the following composition:[5]—

Composition of the Inorganic Matter of Cartilage.

	Per cent.
Carbonate of soda	35·068
Sulphate of soda	24·241
Chloride of sodium	8·231
Phosphate of soda	0·925
Sulphate of potash	1·200
Carbonate of lime	18·372
Phosphate of lime	4·056
Phosphate of magnesia	6·908
Sesquioxide of iron (and loss)	0·999
	100·000

Preparation of Bone-ash.—The best bones for the purpose are stated to be those of sheep and horses, and next, those of calves and oxen.[6] They are calcined with free access of air in a small reverberatory furnace or in a large muffle, until the organic matter which they contain is removed as far as practicable and they become white;

[3] Physiolog. Chem. 1851. 1. p. 413.
[4] Traité de Chimie, 1833. 7. p. 480.
[5] Idem, p. 487.
[6] Anleitung zur berg- und hüttenmännischen Probierkunst. Für Anfänger bearbeitet von Th. Bodemann, Bergprobierer zu Clausthal, auch Lehrer der Probierkunst und analytischen Chemie an der Königlichen Bergschule daselbst. Clausthal, 1845. p. 46.

care being taken not to allow the temperature to become so high as t cause incipient vitrification, or, as Chaudet states, to "porcelainize" them, which would have the effect of making the cupels less absorbent. If the temperature has been too high, the fractured surface of the bones will appear smooth and glassy, and, unlike a sponge, will *not* absorb moisture when touched with a wetted finger.[7] The calcined bones are pulverized; and Chaudet recommends that this should be done by pounding in a very clean iron mortar, and not by grinding between mill-stones, because the bone-ash becomes mixed with the substance of the stones ground off and deteriorated in consequence. The bone-ash is passed through a hair-sieve of medium-sized mesh, and kneaded with water[8] into somewhat flattened cakes about as large as the fist, which cakes are dried and afterwards kept heated to redness in a reverberatory furnace for about two hours. This treatment is necessary in order completely to burn off the organic matter which has escaped combustion in the first calcination; but it often happens that even after the second calcination the carbon resulting from the carbonization of the organic matter is not completely removed, and the cakes are consequently not perfectly white throughout, in which case, after cooling, any portions of the cakes not perfectly white must be separated. The substance of the cakes is passed through the same kind of sieve as previously used, and the powder placed in a tub having a tap inserted at about 15 centimetres from the bottom, and the inner orifice of which is covered with coarse cloth in order to prevent the bone-ash from passing into it and stopping it up. The tub is now filled with boiling water, the contents stirred, and then left at rest for some time, after which the water is drawn off through the tap; and this process is repeated until the water comes away limpid and tasteless. The soluble saline matter, consisting of carbonate of soda and chloride of sodium, is thus removed from the bone-ash. The bone-ash, thus purified by washing, is dried, again pounded, and passed through a silken sieve neither too coarse nor too fine in mesh. If the mesh be too coarse, the pores of the cupel will be much too large and permit silver to pass into the cupel; and if too fine, there will be too much difficulty in separating the last portions of lead and copper; and, besides, cupels too fine in grain are liable to crack and so to cause loss of silver.

The foregoing description of the mode of preparing bone-ash is extracted, and for the most part translated literally, from the excellent treatise on Assaying by Chaudet, who was an assayer in the Paris Mint.[9] We have had much experience in the use of cupels of French manufacture, and we have never seen any so white or better made.

The following remarks are by Bodemann:—Previous to calcination the bones should be repeatedly boiled in water in order to dissolve out as much as possible of the gelatinous matter which they contain

[7] Idem, p. 47.

[8] Chaudet says river-water, which, I presume, must be taken to mean water as pure as can be naturally obtained.

[9] L'Art de l'Essayeur. Paris, 1835 pp. 14 et seq.

and it is suggested that bones so treated may be obtained from manufacturers of glue or size. After the soluble matter has been washed out of the bone-ash, the finest particles of it should be separated by levigation, and collected either by letting them subside or by filtering on a fine linen cloth; and the meal-like powder so obtained should be kept apart, dried, and reserved for coating the cavity of cupels. The grain of bone-ash suitable for cupels should resemble that of coarse wheaten flour. If the grain be too coarse, brightening of the prill will occur sooner, but litharge rich in silver will get into the pores and so vitiate the assay. If, on the other hand, the grain be too fine, the evils previously mentioned will take place, cupellation will proceed too slowly, and a higher temperature than otherwise would be necessary must be maintained. However, too great porosity is a far less evil than too great compactness.[1]

Apatite as a substitute for bone-ash.—The late Mr. David Forbes assured me, in 1856, that he had made excellent cupels of the apatite which he discovered in large quantity in Norway.

Wood-ash as a substitute for bone-ash.—In former times washed wood-ash was exclusively used for cupels; and Bodemann states in his treatise on Assaying, published in 1845, that in Germany cupels continued to be made of wood-ash as well as of bone-ash, and sometimes of a mixture of both. The ash of beech was preferred to that of any other wood, on account, it is suggested, of the larger quantity of phosphoric acid salts which it contains.[2] The ash is to be freed as much as possible by careful sifting from any particles of charcoal which may be present, and then thoroughly washed with water. Should the ash, after this treatment, still retain particles of charcoal, as is usually the case, it must be formed into balls and kept heated to redness, with access of air, until every trace of charcoal is seen to be removed. Instead of pure wood-ash, the ashy residues obtained in soap-boiling before their lixiviation with caustic lime, are used at silver smelting-works, but less frequently in minting establishments. Wood-ash is a worse conductor of heat than bone-ash, and hence cupels made of the former cool less quickly than those made of the latter.[3]

Other substances as substitutes for bone-ash.—They are as follow:—Marl, which consists of carbonate of lime and clay, either by itself or in admixture with wood- or bone-ash; caustic lime and clay, but always in admixture with wood- or bone-ash. According to Bodemann, unexceptionable cupels may be made of the above-named substances; but when a large proportion of marl or clay has been added, they become very liable to crack when heated and in use. A large addition of lime, on the contrary, renders cupels too loose in texture, so as to increase the loss of silver in assaying. A mixture of heavy spar or sulphate of baryta and clay has also been proposed.[4]]

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[1] Op. cit. pp. 46 et seq.

[2] See the Author's volume on Refractory Materials and Fuel, published in 1875, pp. 188 et seq.

[3] Bodemann, op. cit. pp. 48 et seq.

[4] Idem, p. 50. For further information concerning marl, suitable for cupellation, see the Author's volume on the Metallurgy of Lead, 1870, p. 188.

Fluxes, Reducing Agents, and other Materials employed.

Red-Lead.—It should be as pure as can be got; but as it alway contains silver in sensible quantity, this should be estimated an taken into account in returning the assay produce. For this pu pose an intimate mixture of 500 grains of the red-lead and fro 20 to 25 grains of charcoal-powder is heated to low redness in a sma covered earthen crucible for about ten minutes, whereby the lead reduced. The reduced lead, which should weigh about 450 grain is afterwards cupelled, and the button or "prill" of silver weighed From the weight of this button the quantity of silver in the red-lea used in each assay must be calculated, and deducted from the weigh of the silver obtained in the assay.

Litharge is often used instead of red-lead, but the common varieti generally contain more silver than red-lead, the quantity of whic may be estimated in exactly the same manner as in the case red-lead.

Metallic Lead.—Granulated lead and sheet-lead are employe Ordinary commercial lead generally contains too much silver to suitable: the variety known as *assay-lead* is specially made on th large scale by the Pattinson process for assay purposes. Lead ma also be prepared for assaying by heating 10,000 grains of red-lead litharge in admixture with 400 or 500 grains of charcoal-powde Before use, the lead should always be assayed for silver, and th quantity present allowed for: 500 or 1000 grains may be assayed b cupellation direct, or by scorification and subsequent cupellation.

Granulated lead.—Granulated lead is used in scorification. may be prepared by pouring the molten metal into a strong woode box or tray (free from crevices), and rapidly shaking the box or tra until the lead has wholly solidified. It may also be prepared b pouring the molten metal into a large crucible, previously glaze internally, throwing a little charcoal-powder upon it, and stirring th mixture rapidly with a stout stick or iron rod until the lead h solidified. The charcoal-powder is afterwards removed by winnowin or by sifting it through a piece of coarse canvas. The desilverize crystals of lead obtained by the Pattinson process are also employe instead of granulated lead.

Granulated lead may be obtained of any degree of fineness b sifting, but that which passes through a sieve of 16 holes to the line inch is sufficiently fine.

Sheet-lead.—Sheet-lead is chiefly used in the direct cupellation pieces and particles of metal, which are wrapped up in the lead. may be prepared by casting the molten lead, in the mould shown fig. 22, in the form of thin flat ingots, and rolling them out in sheets. In case of emergency a leaden bullet may be hammered o into a sheet.

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[1] The process of cupellation is fully described in the Second Part of Silve Assaying, under the head of Gold-Bullion Assaying, pp. 265 et seq.

CARBONATE OF SODA.—It should be anhydrous, and in powder Bicarbonate of soda may be used, but it is less convenient, as the same bulk contains a smaller quantity of soda. Carbonate of potash may be wholly or partially substituted for carbonate of soda; but it has the disadvantage of deliquescing and of being much dearer.

BORAX.—It should be freed from water by calcination, and in powder.

CHARCOAL.—It should be used in fine powder.

ANTHRACITE.—It should also be finely powdered.

CREAM OF TARTAR OR BITARTRATE OF POTASH.—The commercial varieties, termed *red* and *white argol*, are commonly used: the red argol is preferable, because it has a higher reducing power than white argol, weight for weight.

NITRE OR NITRATE OF POTASH.—It should be in powder. Nitrate of soda may be employed in its stead.

FLUOR-SPAR OR FLUORIDE OF CALCIUM.—It should obviously be free from galena, which always contains silver.

IRON.—Wrought-iron in the form of hoop-iron, rods, strips of sheet-iron or nails, is used in the fusion method in earthen crucibles for ores containing sulphur, arsenic, and lead.

SAMPLING.

Great care is required in sampling silver ores. The various ores and metallurgical products are received by the assayer either in the state of powder in parcels of about half a pound weight, or in lumps of various sizes. If in lumps, these are first broken down into coarse powder, previously to weighing out the sample. It is desirable that the sample should be dried at a temperature of 100° C. to expel moisture, and afterwards reweighed; so that the silver may be returned either upon the moist or dry ore. The sample is then reduced to fine powder in an iron or Wedgwood mortar, and passed through a sieve of 80 holes to the linear inch. The mortar should be covered with a cloth during the process of pounding, to avoid loss.

Frequently a residue of small particles, which on account of their malleability cannot be pounded finer, is left upon the sieve. These particles, which are termed *metallics*, generally consist of metallic silver or chloride of silver, with it may be some bromide or iodide of silver, and native copper: they must be carefully collected, weighed, and put aside to be separately assayed. The sifted sample (without the metallics) is thrown back into the mortar, well triturated, reweighed—to check any carelessness in pounding—and assayed by one of the following methods. [On examining under the microscope the insoluble matter left after boiling a rich silver ore from Valparaiso with nitric acid, and washing with water, I was able instantly to detect particles of chloro-bromide of silver and pick them out with the point of a needle, owing to their softness.—J. P.]

It is impossible to insist too strongly upon the importance of preparing samples of argentiferous ores or products with the greatest care; and by the word "sample" is meant a small portion of a mass

of ore which accurately represents the mean composition of the whole of that mass. Owing to neglect or deficient skill in sampling, we have known more silver paid for in a consignment of ore than the ore contained. The precaution above enjoined with respect to the metallics is essential.

Methods of assaying Ores, Metallurgical Products, etc.

The assaying of a sample may comprise the following operations:—

I. Treatment of the sifted sample by scorification or the fusion method.
II. Cupellation of the resulting button of argentiferous lead.
III. When great accuracy is required, the determination of the silver absorbed along with the litharge by the cupel.
IV. Determination of the silver in the slag produced in the process of scorification or fusion.
V. Assay of the metallics.
VI. Examination of the silver obtained by cupellation for gold.

Two assays at least should be made of each sample.

Scorification.

Scorification is a process which has for its object the removal of every constituent of the ore, except silver, by the solvent action of molten litharge, and the collection of the whole of the silver in alloy with metallic lead. The unoxidized constituents of the ore, such as sulphides and arsenides (except the silver which may be present in such compounds), are oxidized during the process, partly by the direct action of the air, and partly by that of the oxide of lead, which dissolves the resulting products of oxidation; while the oxidized constituents of the ore are simply dissolved in that oxide. Further information on this subject will be found in the Author's volume on the Metallurgy of Lead (pp. 16 et seq.).

All ores, and metallurgical and other products containing silver, may be treated by scorification; but more experience is required to obtain correct results than by some of the fusion methods. Scorification is not, however, so well adapted for assaying substances poor in silver, as the quantity of material operated upon is comparatively small: though this objection may be obviated by concentrating the silver obtained in several scorifications into one button of lead, in the matter hereafter explained.

The process of scorification is conducted in a scorifier placed in a muffle, at a temperature higher than is required for cupellation; and in the following manner. There are weighed out

Sifted ore (or regulus)	50	grains
Granulated lead	500 to 1000	„
Borax	5	„

The ore is mixed in the scorifier with about half of the lead (the

atula, B, fig. 21, being a convenient instrument for the purpose); e mixture is levelled, the remainder of the lead spread evenly over , and the borax placed on the top; the object of the borax being lessen the corrosion of the scorifier, and to render the slag more quid. The scorifier is then put into the muffle and the door closed ntil fusion has taken place. The door is now partly opened to llow of free ingress of air, the temperature raised, and the process ontinued until the surface of the molten lead is covered; the covering onsists chiefly of litharge, but for the sake of brevity will hereafter e termed slag. When the operation, which requires from about half to three-quarters of an hour, is completed, the surface of the contents of the scorifier should be flat and uniform, indicating perfect fusion; and no imperfectly-fused particles should remain attached to the scorifier above the surface of the molten contents.

The slag may be conveniently "cleaned," *i.e.* freed from silver, before withdrawing the scorifier. This is effected by wrapping up from 3 to 5 grains of anthracite-powder in tissue-paper, and dropping the paper on the surface of the slag. The carbon reduces a portion of the litharge, and the reduced globules of lead tend to collect any silver present in the slag, and carry it down with them into the molten lead beneath. When the anthracite-powder has disappeared, and the contents of the scorifier are again in quiet fusion, and the lead is again well covered with slag, the operation may be considered complete.

The scorifier is now withdrawn, and its contents poured into an ingot-mould (fig. 21, c), after which it is put back into the muffle for further use as may be required.

When cold, the slag is detached from the button of lead. The lead should be comparatively soft and malleable, and the button weigh about 200 or 300 grains. The button is then cupelled, the resulting prill of silver weighed, and the weight of silver contained in the lead employed in the scorification deducted, by which means the true weight of silver in 50 grains of ore is obtained.

In the process of scorification, the oxidation of the various constituents of the substance operated upon, which require to be removed —such as sulphur, arsenic, antimony, and copper—is, as previously stated, effected partly by the direct action of the air, and partly by that of the oxide of lead formed by atmospheric oxidation. This part of the process is occasionally accompanied by some effervescence and consequent spirting. Afterwards the oxidation of the lead still continues until its surface is completely covered, and the oxide of lead has formed fusible compounds with the silica and other earthy matters, and metallic oxides. The silver, with any gold which may be present, passes into the unoxidized lead at the bottom of the scorifier.

The quantity of lead required varies with the nature of the substance to be assayed. About ten times the weight of the ore taken is generally sufficient; but 20 or 30 times its weight is sometimes required. In the case of argentiferous lead ores, 50 or 100 grains of the ore may be scorified with only 250 or 500 grains of lead. In the

case of argentiferous copper ores or regulus, 50 grains should be scorified with 750 or 1000 grains of lead: fusion readily occurs, as oxide of copper forms very fusible compounds with oxide of lead. Where a large number of assays have to be made, instead of weighing the granulated lead, it is measured by the copper ladle, A, fig. 18.

If the button of lead be hard from the presence of copper, antimoney, or other substance, or if it be too heavy for the cupel, it should be replaced in the same hot scorifier, with an additional quantity of lead if the button be too hard, and the scorification continued sufficiently long to obtain a button of the requisite size and softness. There is no loss of time in re-scorifying, and it ensures the lead being sufficiently pure to "pass the cupel" (*i.e.* to be properly absorbed by the cupel); unless this is the case, scoria may be formed on the surface of the cupel, and lead to an incorrect result.

The temperature should be well maintained during the process; if too low at first, silver is liable to be retained in the slag, and cannot afterwards be completely extracted. The formation of white spots (due chiefly to sulphate of protoxide of lead) on the surface of the slag generally indicates that the temperature has been too low. If the slag appears pasty when the temperature is sufficiently high, borax is added at intervals in quantities of 5, 10, or 20 grains at a time. The borax may be conveniently wrapped up in tissue paper and allowed to fall on the surface of the slag. It is not advisable to introduce more than a few grains of borax at the commencement of the operation, as it would melt, cover the surface of the lead, and retard its oxidation. If any imperfectly-fused particles are present in the slag or on the scorifier, notwithstanding the temperature has been sufficiently high, the assay must be repeated with the addition of more lead.

When the substance to be assayed is poor in silver, it is usual to weigh out 6, 12, or more portions of 50 grains each, and to scorify each portion separately and simultaneously; the resulting buttons of lead are re-scorified, two or more together; and this process is repeated until the whole of the silver is concentrated in one button of lead, which is then cupelled. One simple assay by the fusion or *pot* method would often be preferable; but in some metallurgical works it is considered inexpedient to deviate from the customary practice of the works.

Instead of cleaning the slag by anthracite-powder during scorification, it may be treated in an air-furnace in the manner to be subsequently described (see p. 246).

Fusion or Pot Method.

This method of assaying varies somewhat according to the nature of the substance to be operated upon, and will, therefore, be described under several heads.

Assay of Silver Ores.—The following process is applicable to all silver ores consisting chiefly of rock or vein-stuff, and containing only a small proportion of other metals, such as copper and antimony

and the majority of samples of silver ore are so constituted. The following proportions are taken:—

Ore	100 to 500 grains (according to richness in silver).	
Red-lead	500	„
Charcoal-powder	20 to 25	„
Carbonate of soda and Borax.....	500	„ together.

Carbonate of soda being a flux for silica and silicates, and borax for lime, oxide of iron, and other bases, the relative quantities of the two must be varied according to the nature of the ore. A mixture of equal weights usually answers very well. If sulphate of baryta or of lime, or phosphate of lime be present, fluor-spar may be added with advantage. The assay may be made in an earthen crucible, fig. 11, or in an iron crucible, fig. 12, p. 229.

The ingredients (excepting a small part of the borax) are well mixed together, either in a mortar or on the assay-scoop, and then transferred to the crucible, or they may be mixed in the crucible itself. The mixture is covered with the remainder of the borax, reserved for that purpose. The crucible is heated in an air-furnace until effervescence has ceased, and the contents have become thoroughly liquid and tranquil. The temperature should not be raised too rapidly at first, as the fine globules of reduced lead may subside and collect at the bottom of the crucible, before the silver is completely reduced, and therefore without carrying the whole of it down along with them.

When fusion is completed, which occurs in about 15 or 20 minutes, the crucible is withdrawn from the furnace, its contents poured into an ingot-mould, C or D, fig. 21, and allowed to cool. The slag is afterwards detached from the button of lead, which should be soft and malleable, and weigh from 350 to 450 grains. The button of lead is cupelled, and the silver in the ore estimated in the manner and with the precautions previously mentioned.

Occasionally the button of lead is somewhat brittle, or accompanied by a regulus, owing to the presence of galena, iron-pyrites, or some compound of copper, antimony, or arsenic, in which latter case it would yield an erroneous result. The best remedy in each particular case must be left to the judgment and experience of the assayer; but the following observations on this subject may prove useful.

If sulphur or arsenic be present, they may be generally to a great extent eliminated by previously roasting the ore.

If the button be brittle and resemble sulphide of lead in colour, either galena or iron-pyrites was probably present in the sample. The addition of metallic iron, during the fusion, will decompose the sulphide of lead, and yield a soft and malleable button.

When arsenic is present, iron will decompose the arsenical compound with the formation of a speise, which separates as a hard, greyish-white layer on the surface of the button of lead.

When sulphides are present, the proportion of red-lead should

be increased, by which means the sulphur will be oxidized, and the formation of regulus prevented. If the button of lead obtained be inconveniently large, a small quantity of nitre may be added instead of increasing the proportion of red-lead, and the charcoal be omitted.

If the button be brittle, comparatively hard, and white, it generally contains antimony, in which case nitre should be added; the proportion required will vary with the quantity of antimony present; it may be so adjusted that a malleable button free from antimony will be obtained (see p. 247).

The slag, which is generally glassy, varies much in colour according to the nature of the ore: it should be uniform in colour and structure; not streaked or variegated, as that generally indicates that the mixture has been imperfectly fused.

Cleaning the slag.—The slag is collected, roughly powdered, and "cleaned" in the following way:—It is mixed with from 300 to 500 grains of red-lead, from 15 to 25 grains of charcoal-powder, and from 30 to 50 grains of carbonate of soda; and kept melted for 10 or 15 minutes in the crucible previously used for the fusion. If the fused product be thick and pasty, the proportion of carbonate of soda should be increased or borax added. The contents of the crucible are poured into a mould, the slag detached from the button of lead and thrown away, and the latter cupelled either by itself or with the assay-button previously obtained.

The preceding description of the method of cleaning the slag is applicable to all ores and products, which are assayed for silver. The richer the ore, the more needful is it to clean the slag; in the case of poor ores it may generally be omitted. However, in the case of a description of ore with which the assayer is not familiar, it is better not to omit the examination of the slag, until experience has shown that this may safely be done.

Assay of Argentiferous Copper Ores or Regulus by the Fusion Method.—These substances are often very troublesome to assay correctly by the fusion method, as they are generally poor in silver, and contain a large proportion of copper. Sulphide of copper is decomposed by oxide of lead, the sulphur and a part of the copper being oxidized; the rest of the copper passes into the reduced lead, and the button of lead is frequently inconveniently large for cupellation. Moreover, it is necessary to add enough oxide of lead, not only to collect the silver and oxidize the whole of the sulphur present, but to yield a button of lead sufficiently large to carry properly all the copper present in the button of lead into the cupel. One part by weight of copper requires about 16 parts of lead for cupellation; and though a smaller quantity of lead will pass the copper into the cupel, yet a sensible amount of silver would in that case accompany the lead and copper, so that an incorrect result would be obtained.

If the fusion method be employed, the substance may be assayed either (*a*) raw; (*b*) after calcination; or (*c*) after previous treatment with acid.

(*a*) In the case of raw ores or regulus, the following proportions may be taken :—

Ore or regulus....	100 to 500	grains (according to richness in silver).
Red-lead.....	2000 to 3000	„
Charcoal-powder..	15 to 35	„
Siliceous sand....	100 to 250	„

But if the quantity of sulphur to be oxidized be large, the charcoal may be omitted, as sufficient lead will be reduced without it; and in some cases a little nitre should be added to the mixture to assist in oxidizing the sulphur, etc. Fusion may be effected in an earthen or iron crucible at a comparatively low temperature; and the resulting button of cupriferous lead, which should weigh not less than 450 grains, is cupelled. The sand is added to diminish the action of the oxides of lead and copper upon the earthen crucible; if an iron crucible be used, the sand may be left out.

(*b*) The sample may be calcined either in a roasting dish, or in the crucible to be subsequently used for the fusion. The quantity to be assayed should be weighed out before calcination. The following proportions are taken :—

Ore or regulus....	100 to 500	grains (according to richness in silver).
Red-lead	1000	„
Charcoal-powder..	35	„
Carbonate of soda.	200 to 300	„
Borax.....	150 to 300	„

The fusion is made as in (*a*).

The slag obtained by either (*a*) or (*b*) is generally vitreous and red from the presence of cuprous oxide. It is "cleaned" in the manner previously described.

(*c*) The following method may be conveniently employed as a check upon other methods:—100 grains of the sample (or more, if it be poor in silver) are heated in a flask with strong nitric acid, or a mixture of sulphuric and nitric acids; and to the solution diluted with water, a little hydrochloric acid or salt is added to precipitate the silver, after which the solution is filtered. The filtrate, which should be bright and clear, contains the copper, and may be neglected. The residue, containing the silver, is dried, gently ignited, and mixed with the following substances:—

Red-lead.....	300 grains.		
Charcoal-powder.....	15 „		
Carbonate of soda and Borax	varying up to	300 „	together.

The mixture is fused for 10 or 15 minutes, and the resulting button of lead cupelled. By this method, owing to the absence of copper from the button of lead, the process of cupellation is not liable to be interfered with.

Assay of Grey Antimonial Copper Ore by the Fusion Method.—In the case of an antimonial copper ore, containing about 30% of

copper and 150 ozs. of silver to the ton, the following proportions have been found suitable for making an assay by the fusion method :—

Ore	100 grains.
Red-lead	500 „
Carbonate of soda	400 „
Nitre	60 „

The mixture was fused in an earthen crucible, when effervescence occurred. The resulting button of lead was sufficiently free from antimony to be cupelled direct; no scoria was formed on the surface of the cupel, and practically the whole of the silver was contained in the assay-button.

Assay of Argentiferous Lead Ores by the Fusion Method.—The assay of ores rich in lead has been fully described in the Author's volume on the Metallurgy of Lead.

Ores comparatively poor in lead may be assayed for silver by the fusion method, which is generally preferable to scorification for such ores. The following proportions are taken :—

Ore	300 to 500 grains.
Red-lead	300 „
Charcoal-powder	15 „

Fusion is effected in an iron crucible, or, with the addition of a piece of iron, in an earthen crucible.

The button of lead is cupelled, and the slag cleaned in the usual way.

In the case of lead ores, the silver is generally calculated in ounces per ton upon the lead in the ore as determined by dry assay, instead of upon the ore itself.

Assay of the Metallic Residue obtained by sifting the powdered Sample.

The "metallics" or unpulverizable metallic residue may be assayed by cupellation direct, or by scorification and cupellation, or by fusion and cupellation.

For cupellation direct, the residue should be small : it is rolled up in a convenient weighed quantity of sheet-lead, and then cupelled.

For scorification, it may be mixed with about 250 grains of lead, with the addition of a little carbonate of soda, if chloride of silver be present.

For fusion, it may be mixed with 300 grains of red-lead, 15 or 20 grains of charcoal-powder, and a small quantity of carbonate of soda and borax ; the mixture should be kept melted for 10 or 15 minutes.

When the metallic residue is considerable, larger quantities of reagents should be used.

Estimation of the Silver in the Cupel.

Absorption by the cupel. — The small quantity absorbed by the cupel need only be estimated when great exactness is required, and this may be done in the following way :—The white portion of the cupel is broken off and rejected ; the stained portion is powdered and mixed with sufficient charcoal-powder to reduce all the litharge

(*i.e.*, 4 or 5 parts by weight of charcoal for every 100 parts of litharge), and with from 100 to 250 grains of fluor-spar, of borax (or glass free from lead), and of carbonate of soda, respectively. If the oxide of lead in the cupel be small, it is advisable to add 300 grains of red-lead and an additional 15 grains of charcoal-powder to the mixture. The mixture is fused in an earthen crucible in an air-furnace, and the resulting button of lead cupelled. If the button of silver thus obtained be comparatively large, the cupel used in this case should be examined for silver in the same way, and even a third or fourth cupel may be similarly treated. But generally the quantity of silver in the second cupel may be disregarded.

To save time and labour the powdered stained portion of the cupel may be added to the uncleaned slag and any regulus or scoria, and the whole assayed for silver by fusion with 20 or 30 grains of charcoal-powder, with or without the addition of fluxes, as circumstances may require.

The loss of silver by volatilization during cupellation is very slight (unless the temperature has been much too high), and may be disregarded.

Examination of the Silver "Prills" for Gold.

Gold is not unfrequently present in sensible quantity in argentiferous ores from California, South America, and some other localities, and in argentiferous regulus; and it should always be looked for.

One or more of the "prills" are flattened out by hammering, and heated with dilute nitric acid; the solution is poured off, and the residue treated with stronger nitric acid: the gold, which is thus usually left in the form of a black or brown powder, is washed, dried, ignited, and weighed.

See note on estimation of silver in lead at p. 296.

THE METHOD OF ASSAYING SILVER ORES AT ONE OF THE LARGEST LEAD-SMELTING WORKS IN GREAT BRITAIN.

The following terse description has been written, at my request, by my friend Mr. Allan Dick, who has had, amongst other duties, the charge of the assay and smelting department of one of the largest and most important lead and silver smelting-works in North Wales; and his directions will be found eminently practical. It is not to be supposed that, in assaying silver ores at all metallurgical works, the elaborate precautions are observed which are prescribed in the foregoing article on the subject by Mr. Richard Smith, who is engaged in teaching the art of assaying to the students in the Metallurgical Laboratory of the Royal School of Mines; though it may be desirable, by way of scientific training, to communicate to such students information of the most precise and accurate kind. An assayer who possesses the requisite aptitude for manipulation, soon acquires the skill which enables him to dispense with the tedious process of weighing out all his reagents.

Generally one assayer and an assistant are employed, and there are two melting-fires (air-furnaces, like that previously described) and one muffle-furnace, about a dozen jars containing fluxes, etc., two balances, and sundry tongs, pokers, and shovels. Gas-coke is the fuel used. The balance for weighing ore should turn freely with half a grain when each scale is loaded with 1000 grains. The other balance, for general purposes, should turn with 1 grain when each pan is loaded with 1 lb. In another room is the assay-balance for weighing the silver obtained, which should be capable of turning with 0·001 of a grain when the pans are loaded with 20 or 30 grains each.

Of course everything depends upon the method, skill, and care of the assayer and his assistant. They are brought up to the work, and usually begin about thirteen years of age, earning then five or six shillings per week; they carry in fuel, riddle bone-ashes, clean up, mix fluxes, grind ores, assay slags, and eventually ores. As they get older they can stick to work all day and all night too, if needed. They then get about twenty shillings a week, and something more when there is overtime and business is brisk.

The ores are ground, sifted, and mixed by the seller before being sampled. The sieve is such as will allow nothing larger than coarse sand to go through. If any metallic silver is stopped, it is cut up with scissors and thrown into the bulk. Two samples are sent from each lot to each intending bidder for such ores. Each sample weighs about 8 ozs., sometimes 10 or 12 ozs.

When the samples arrive in the assay-room, they are put out upon a table in order and inspected. An assay is then made of each sample, so that two assays are made of each lot. The method is as follows:—

The whole of each sample is put into a sieve about 9 inches in diameter and 3 inches deep. The sieve is made of the finest brass wire-gauze. It is bumped and shaken till no more goes through. The coarser part is then put into a brass mortar standing on the floor, and stamped by an iron pestle about a yard in length, which passes through a piece of stiff leather covering the mortar. The pounded ore is again thrown on the sieve: the coarser part again stamped, and so on till all has gone through the sieve, or until it is evident that what remains is malleable. The malleable part, which is called "metallics," is put in a paper, folded up, and laid by the side of the sample. When all the samples have been so treated, they are arranged and inspected once more.

The next part of the work is the "leading" of the "metallics" and samples. The assayer manages the two fires, which are placed about a yard apart, whilst his assistant does the weighing and mixing. All must go on with the regularity of clockwork.

The crucibles used are of wrought-iron, such as are employed for lead-assaying: the first sample of each lot is "leaded" in the right-hand fire, and the second sample in the left-hand fire, or *vice versâ*.

Whilst the assayer gets his fires and crucibles ready, his assistant

weighs the whole bulk of each sample from which any "metallics" have been sifted out. He also weighs the "metallics" and records all the weights. He then takes the "metallics" of the first sample and mixes them on a copper scoop with about an ounce of litharge, some black flux, carbonate of soda, and red tartar (*i.e.* red argol or common cream of tartar). His measure is a teaspoon. He then hands the scoop to the assayer if he is ready; if not, the assistant lays it down on its appointed spot close to the assayer's hand, who shoots its contents into the red-hot crucible and sweeps with a hare's foot any particles left in the scoop into the crucible. The crucible is then plunged into the right-hand fire and more or less covered with a wrought-iron lid. More fuel is added to the fire if need be. By this time the assistant has got the "metallics" of the second sample mixed on its scoop and placed in its position. The assayer then turns his attention to the left-hand fire, and gets the second "metallics" into that—keeping his eye on the first all the while. Having arranged the crucible in the second fire, he takes out the first crucible when it is ready and pours its contents into a conical mould, taps the crucible to collect the lead remaining in it into a prill, which he jerks out and places beside the mould. The mould is then carried away by his assistant, and made to stand in water to make sure that the lead has set: it is next inverted on a board in its proper place, with the little prill alongside; on raising it up the button of lead with the slag attached is left on the board. The first "metallics" are then said to be "leaded." The moment the prill is jerked out, the assayer cleans the crucible and shoots the next mixture into it, arranges it in the right-hand fire, adds fuel if need be, and turns his attention to the crucible in the left-hand fire, the contents of which are now ready to pour out, and so on till all the "metallics" are "leaded" and arranged on the board in their proper places.

The "leading" of the samples then begins; each one being again carefully mixed before weighing out the portion for assay.

The weights employed are very various. The weight most commonly used in North Wales is a special weight called a "silver assay-ounce." Its exact weight is 408⅓ grains. It is not a standard weight, but a fraction of a ton.

This silver assay-ounce is divided into half and quarter assay-ounces. The weight of sample generally taken is a quarter assay-ounce. It is mixed with 1½ or 2 ozs. of litharge; at some smelting-works 1½ oz. and at others 2 ozs. being used. The mixture of ore, litharge, black flux, red tartar, and carbonate of soda is made as before on the scoop, and "topped up" with carbonate of soda; generally a little pounded fluor-spar is added.

The "leading" of the samples is carried out in the same systematic manner as in the case of the "metallics."

The slags are then knocked off from the "leads" (*i.e.*, argentiferous buttons of lead obtained). If any samples yield *hard metal* "speise," they may be examined for copper, nickel, and cobalt, if the lot is a large one. The "leads" are then cleaned by wet hammering

and dried on a hot iron plate; the *prill* is driven into each *lead*, so as to go with it into the test (*i.e.* cupel).

The "leads" are then weighed. If the weight is short, the sample is re-assayed; if too heavy, the sample is tried for lead.

The tests or cupels are arranged in a large muffle heated by flame, so that from 20 to 40 stand in the centre of the floor of the muffle, all at about the same heat. The "leads" are put into the tests after these have been red-hot half an hour. When the cupellation is over, the tests are withdrawn in order and inspected, to form an idea of the coppery or antimonial nature of the ores. Their arsenical nature has been already judged of from the presence or absence of *hard metal* "speise."

The prills of silver are weighed by the owner of the works or manager, or other person. From the weight of the prill in grains and decimals of a grain, the produce is easily calculated: and the weigher at once enters in his assay-book the ozs. and dwts. of silver per ton of ore.

Example.—If a silver assay-ounce, 408⅓ grains, yields a prill weighing 1 grain, that will correspond to 80 ozs. of silver per ton,

since 408·3 : 1 :: (2240 lbs. × 7000 grs. =) 15680000 : 80
∴ 10·0 grain prill equals 800 ozs. per ton,
1·0 „ „ 80 „ „
0·1 „ „ 8 „ „
0·01 „ „ 16 dwts.,
0·005 „ „ 8 „
and so on.

If the quarter assay-ounce is used, the weight of each prill must be multiplied by 4.

The "metallics" are cupelled and the amount of silver per ton added to that obtained by assay of the sifted sample—only instead of being from a quarter assay-ounce of ore, the weight of prill is from 8, 10, or 12 ozs., or whatever the whole sample weighed. The ores are then valued, and an offer per ton submitted to the seller or his agent. If the two assays of each sample do not agree within reasonable limits, two re-trials of each lot (one of each sample) are made.

When the ore yields very impure lead buttons, the test is generally pounded up, mixed with some pounded fluor-spar and the slag from its direct assay. This mixture is again "run down" in the iron crucible with some tartar. The silver absorbed is thus obtained by cupellation of the resulting lead. This is also done when there is time with all unusually rich ores. Imported silver ores average about 250 to 300 ozs. of silver per ton, but run up to 3000 or 4000 ozs. and down to 50 ozs. per ton.

The weight of litharge employed is large enough to yield sufficient lead to work on the test without scorification, except in rare cases, and the mixture of fluxes with the iron of the crucible suits all sorts of ores and furnace products, and will do for a quarter, half, or whole assay-ounce trial, unless very coppery.

SECOND PART OF SILVER-ASSAYING.
(ASSAY OF GOLD AND SILVER BULLION, COIN, AND PLATE.)

Balance, Furnace, and Implements.

Balance and Weights.—An assay-balance usually has a skeleton beam from 8 to 10 inches in length, the weight of which should not exceed 250 grains, while some of the best beams weigh only about 70 or 80 grains: such a balance should at all times distinctly indicate $\frac{1}{10000}$th of a grain when loaded with 10 grains in each pan. It should be so constructed that, when equal weights are put in the two pans, the index needle stands at zero, and this state of equilibrium is not disturbed when the weights are transposed; but as this condition involves an absolute equality in the length of the arms (which it is impossible to maintain permanently), Mr. G. Foord,[1] of the Royal Mint at Melbourne, has recently suggested a modification of the well-known system of double weighing which eliminates any error arising from this source, and in which the initial and final weighings are conducted with the same total load in each pan. The method certainly has considerable advantages, but the large number of weights required (unless some confusing calculations are gone through) will probably prevent its coming into general use, for the mark on a weight does not indicate its actual weight, but 990-thousandths minus its actual weight in thousandths; hence no less than 100 weights, supplemented by a rider weighing 10-thousandths, are needed to complete the series from 1 to 1000.

Whatever method of weighing be adopted, the index of the balance moves over a graduated ivory scale. The divisions on it, and the position of the centre of gravity of the beam, are so correlated, that an excess of $\frac{1}{10000}$th part of the assay-pound in either pan is equivalent to 1 division on the scale. When such a relation exists, it is not usual to adjust the metal to be assayed to the exact weight, as time may be saved by recording on the assay-paper the variation in weight in terms of the divisions on the scale; but the assayer should never permit a greater variation than + or — $\frac{4}{10000}$th parts. This amount is subtracted from or added to (according as it is positive or negative) the weight of the pure metal finally obtained, in order to ascertain the exact weight of gold per thousand parts. By so doing, alloy is evidently reckoned to be pure gold, but the error introduced is quite insignificant.

The unit of weight, termed the "assay-pound," varies with the practice of the operator from 5 to 16 grains, and the subsidiary weights usually bear a decimal relation to it. Gold assays made for the trade, however, are frequently reported on the old system of

[1] On a proposed New Method of Weighing applicable to the Gold Bullion Assay. By G. Foord. Read before the Royal Society of Victoria, 8th Nov. 1875.

"carats," "carat-grains," "eighths," and "excess-grains." The relation between these subdivisions of the assay-pound will be at once evident from the following table:—

				Excess-grains.	Decimal equivalent.
			Eighths.	1	0·1736
		Carat-grains.	1	7·5	1·3021
	Carats.	1	8	60	10·416
Assay-pound.	1	4	32	240	41·6
1	24	96	768	5760	1000·0

It will be seen that the terms, carat, carat-grain, eighth, and excess-grain, represent proportional parts of the assay-pound; the excess-grain bearing the same relation to the assay-pound, as the troy grain to the troy pound. The term, excess-grain, seems to have originated from the fact that some assayers are accustomed to report only the number of carats, carat-grains, and eighths of gold contained in bullion; and, as each eighth represents 7·5 grains in a troy pound, each $\frac{1}{75}$th of an eighth *in excess* will be equivalent to 1 troy grain per pound *in excess* of the report.

The total number of "excess-grains" in the assay-pound is the same as the number of troy grains in a troy pound, an arrangement which materially assists in subsequent calculations for adjusting the bullion to any required standard.

In assaying silver by cupellation a decimal series of weights may be employed, but trade reports are given in "ounces," "pennyweights," and "excess-grains," the assay-pound being usually 12 grains. These subdivisions are related in the manner indicated in the following table:—

			Excess-grains.	Decimal equivalent.
		Pennyweights.	1	0·1736
	Ounces.	1	24	4·16
Assay-pound.	1	20	480	83·3
1	12	240	5760	1000·0

It will be evident that since the ounces, pennyweights, and excess-grains in the table, represent the same proportional parts of the assay-pound, as troy ounces, pennyweights, and grains of the troy pound, a report on this system indicates the amount of precious metal present in a troy pound in troy ounces, pennyweights, and grains without calculation.

In this country the proportion of gold or silver in ingots or bars is always referred to the legal coin-and-plate "standards" for the two metals. Thus, gold coin contains in 24 parts, 22 of gold, and 2 of alloy; these parts are called carats, the gold carat containing 4 grs. and the grain being subdivided into 8 parts. The "standard" for silver coin and plate consists of 11 ozs. 2 dwts. of silver, and 18 dwts. of copper in the pound, or 12 ounces troy. The conventional terms, "betterness" and "worseness," are used to show how much gold in carats, grains, and eighths, and how much silver in ounces and pennyweights, the ingots contain more or less than the legal "standard," the money-value of which is always known.

A less cumbrous method consists in showing how many parts either of gold or silver are contained in 1000 parts of the ingot: the above legal "standards," converted into 1000ths, being represented by the numbers 916·66 for gold, and 925 for silver.

Examples.—Thus, if a specimen of gold bullion were taken for assay, weighing 24 carats, and the "cornet," after applying all necessary corrections, weighed 23 carats 3 ct. grs. (abbreviation for carat-grains) 3 eighths and 3 ex. grs. (abbreviation for excess-grains), the metal would be reported as B^{r}. (abbreviation for Better) 1 ct. 3 ct. grs. 3 eighths and 3 ex. grs., the decimal equivalent of which is 994·0. A poor alloy, giving on assay 20 cts. 0 ct. gr. 5 eighths and 3 ex. grs. would, however, be reported as W. (abbreviation for Worse) 1 ct. 3 ct. grs. 3 eighths and 3 ex. grs., since the report is, in all cases, required to give the amount by which the metal differs from standard, 22–carat, gold: the decimal equivalent of this report is 840·4.

It should be carefully noted that in both high and low standards the excess-grains indicate an amount of gold present *in excess* of the report, so that whether in conjunction with Betterness or Worseness they always indicate betterness. Hence the report W. 1 ct. 3 ct. grs. 3 eighths 3 ex. grs. means that the alloy is richer than the report W. 1 ct. 3 ct. grs. 3 eighths would indicate by 3 grains per pound: this fact is shown by the amount by which the above actual weight differs from 22 cts. These explanations apply with equal force to the assay of silver.

Furnace in use at the Royal Mint.—Fig. 24 represents a front elevation and fig. 25 a section of the furnace used in the Royal Mint. It is formed externally of wrought-iron plates about $\frac{1}{8}$ of an inch thick, united by angle iron. This casing is connected with a chimney 60 feet high by means of a wrought-iron hood *a*, and flue, which is provided with a damper *b*. The furnace is lined with red Windsor bricks, and has five openings, all in the front, as shown in fig. 24. Fuel is introduced through the largest of these under the flap *c*, the position of which

may be adjusted by means of two indented inclined planes. The opening *d* communicates directly with the muffle *e*, and may be closed by sliding doors *f f'*, or by a plumbago or firebrick front *g* in conjunction with the sliding plate *h*. The openings *j j'* are for introducing and withdrawing the furnace-bars, and are occasionally employed in regulating the draught, for which latter purpose the

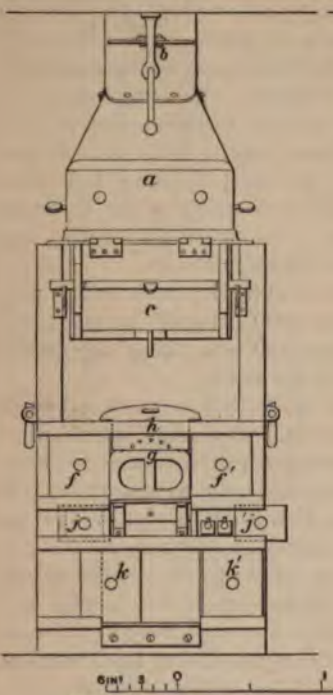


Fig. 24. Front elevation.

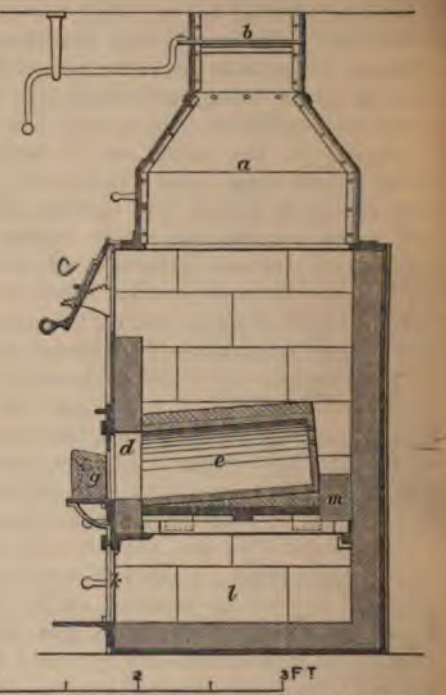


Fig. 25. Vertical section parallel to the axis of the muffle.

Fig. 24A. Vertical cross-section of the muffle. The dotted line shows the thickness of the clay coating.

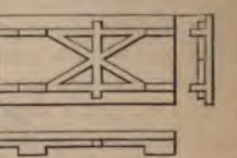


Fig. 25A. Girder-plate. Plan of the under-surface; end and side elevations.

Assay-furnace at the Royal Mint.

doors *k k'* of the ash-pit *l* are usually employed. The muffle, a front elevation of which is shown at fig. 24A, is usually formed of fire-clay, but occasionally of plumbago or cast-iron, and is provided with four openings at the upper part of the closed end, by means of which a draught is established: these slope from within downwards, in order to prevent particles of fuel finding their way into the muffle.

re are nine firebars, but only the two outer ones on each side are covered with fuel. On the other five bars rests what is termed the girder-plate, which is of cast-iron and shown in section in fig. 25. This plate is flat on the upper surface, but has rib-like projections on the under-surface, in order to prevent buckling (see fig. 25A). Over the girder-plate the muffle is fixed in an inclined position, so that all the cupels may be visible from the front. The inclination is given by covering the girder-plate with a layer of bits of fire-brick, plastered over with fire-clay, in the manner shown in fig. 25. It will be per-

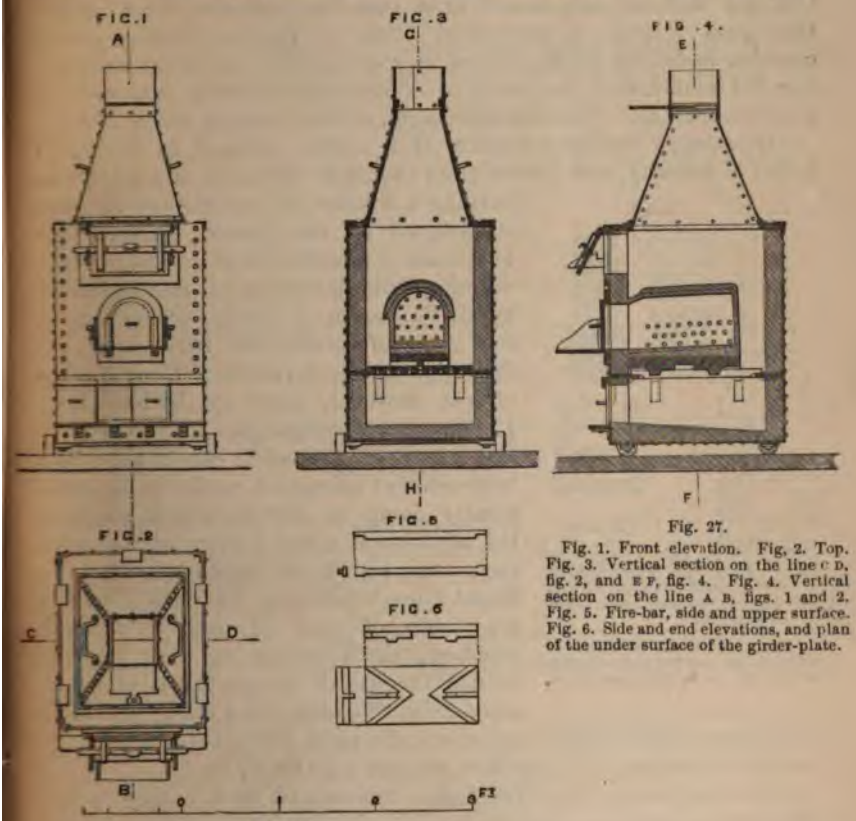


Fig. 27.

Fig. 1. Front elevation. Fig. 2. Top. Fig. 3. Vertical section on the line C D, fig. 2, and E F, fig. 4. Fig. 4. Vertical section on the line A B, figs. 1 and 2. Fig. 5. Fire-bar, side and upper surface. Fig. 6. Side and end elevations, and plan of the under surface of the girder-plate.

Fig. 26.

Assay-furnace at the Japanese Mint.

ceived that the fire-grate, properly so-called, consists only of four bars, the other five bars under the muffle serving only to support the girder-plate. It is convenient to cover the top of the muffle with a thick luting, composed of fire-clay and a little graphite, in order to check radiation and to protect the muffle, and a firebrick, *m*, is placed behind to prevent excessive heat. Charcoal, anthracite, and coke are fuels suitable for this class of furnace; but, on account of expense, the first is now rarely employed, and in the Royal Mint anthracite is always used.

A form of assay-furnace, which may be considered a modification of that above described, and which was constructed for the Hong Kong Mint and is in use at the Japanese Mint, is shown in figs. 26 and 27.

Gas Assay-furnaces.—An assay-furnace in which gas is employed as fuel has been designed by Mr. A. J. Watson, of the Sheffield Assay Office, where it has for some years given satisfactory results. The muffle is slightly smaller than that shown in fig. 25, and, extending like a tunnel through the furnace, may be opened at either end. Coal-gas and air are mixed in a cast-iron cylinder, from which they pass through a perforated block of firestone into a small chamber under the muffle, where they are ignited, the flame enveloping the muffle, and the products of combustion being removed by a contracted flue. (For the description of this furnace, see p. 296.)

Wiesnegg's furnace[1] consists of a muffle enclosed in a double jacket of fire-clay, and heated from the back by means of six twyers, burning a mixture of coal-gas and air, and constructed on the Perrot system: the temperature produced is stated to be very uniform. Similar furnaces, manufactured by M. Th. Issem, of Berlin, are in use in the Mints of Berlin and Utrecht, where they give excellent results. The pressure of gas, however, must not be less than 12 mm. on a water-gauge.

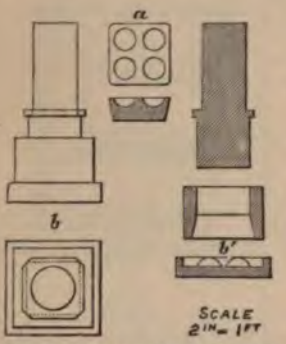


Fig. 28. Plate-cupel (*a*) in plan and section; and mould (*b*, *b'*), *b* in elevation and plan, and *b'* in vertical section.

The mould, it will be seen, is in three pieces, and the plate-cupel is formed with the cavities downwards.

Cupels.—In preparing cupels, the finest bone-ash is moistened until it is sufficiently damp to cohere (which requires the addition of about 1 ounce of water to each troy pound of bone-ash). In the Royal Mint, where large numbers of assays are made of gold of nearly uniform standard, much saving of time has attended the use of square plates of bone-ash (*a*, fig. 28), each plate being provided with four circular cavities in which the assay-pieces[2] are placed. A mould for making such cupels is represented at *b*, *b'*, fig. 28.

Furnace Tongs, etc.—The tongs represented at *a*, *b*, fig. 29, are used for manipulating the cupels: *b* is also employed for introducing the assay-pieces into the cupels; *c* is a rotating support or "peel" for introducing the platinum tray, fig. 39, page 263, into the muffle. It is shown in plan and side elevation. It consists, as will be seen, of four arms, turned up at the ends so as to hold the tray securely. The platinum tray, with its cups and cornets, is placed upon the peel, in the position indicated by the dotted lines. In order that all the

[1] Constructed by M. Wiesnegg, of 64 Rue Gay-Lussac, Paris.

[2] This term is generally to be understood to apply to the portion of alloy selected and weighed ready for assay; but in some cases (as in the present) it includes the silver and lead which are cupelled with the portion of alloy.

cornets may be heated to the same temperature, the tray is made to rotate while in the muffle, by pulling it with the instrument F, fig. 39. Another form of peel is represented at E, fig. 39. Messrs. Johnson, Matthey, and Co. use a peel with only three arms, which rotate over a disk of iron, smaller in diameter than the circle described by the ends of the arms; and they insert between the tray and the peel a

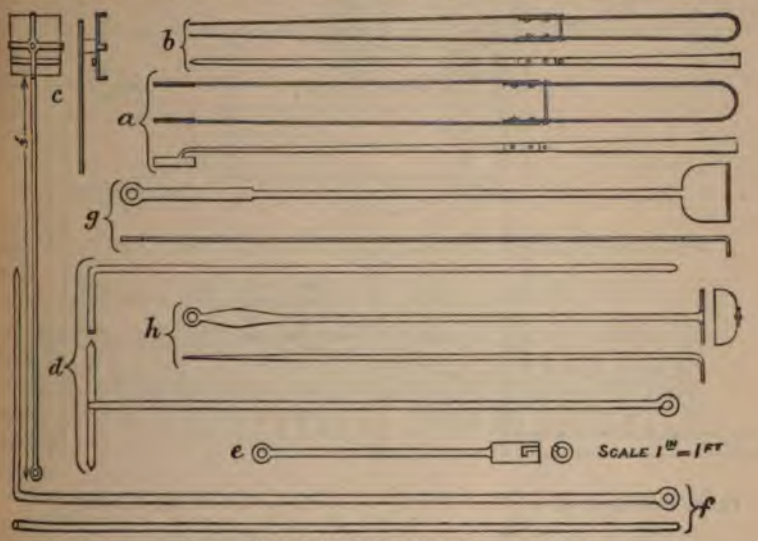



Fig. 29. Furnace implements.

loose disk of sheet platinum, with a view to prevent the possibility of particles of oxide of iron from the peel getting into the cups. The various tools used in stoking the furnace are represented at *d* and *f*, and those for cleaning out the muffle at *g* and *h*; *e* is the key for pulling out the side bars through the openings *j j'*, fig. 24. The tongs used for lifting the parting-flasks seen in fig. 36, are shown at C, fig. 19 (p. 233).

HAMMERS AND ANVIL.—It is well to have two hammers of the shape shown at fig. 30, the heads of which weigh 7 and 11 lbs. respectively. The anvil should be of cast-steel or of wrought-iron faced with steel; about 5 inches in diameter, 8 inches deep, and firmly fixed in a block of wood. Its face should be polished and kept bright.

Fig. 30. Hammer for flatting buttons.

ROLLING MILL.—The ordinary jewellers' mill (figs. 31–35) is the form usually adopted; but considerable care should be devoted to accuracy of manufacture, as it is of great importance to be able to roll large numbers of strips of metal of the same thickness. The handle should have a radius of not less than 15 inches, and time may be saved by introducing an inclined plane between the two uprights of the mill, by means of which the strips, after passing through, are immediately returned to the side at which they were introduced.

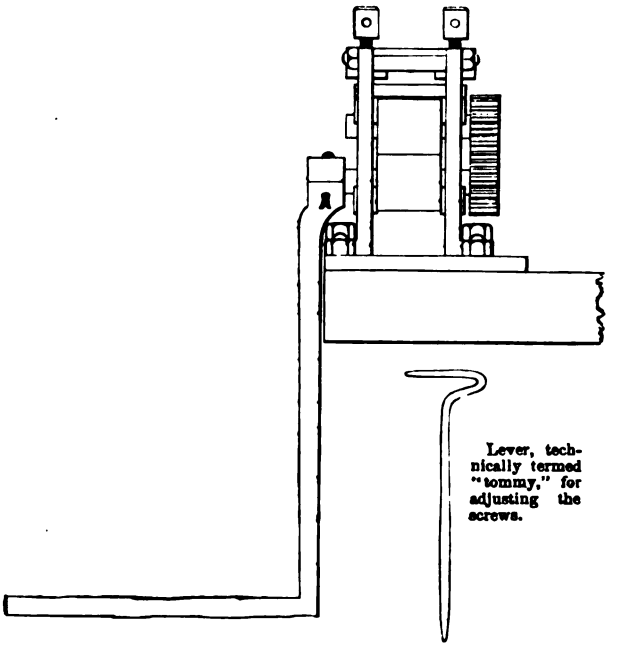


Fig. 31. Front elevation.

Fig. 32. End elevation handle side.

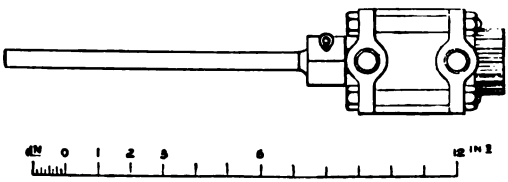


Fig. 33. Plan.

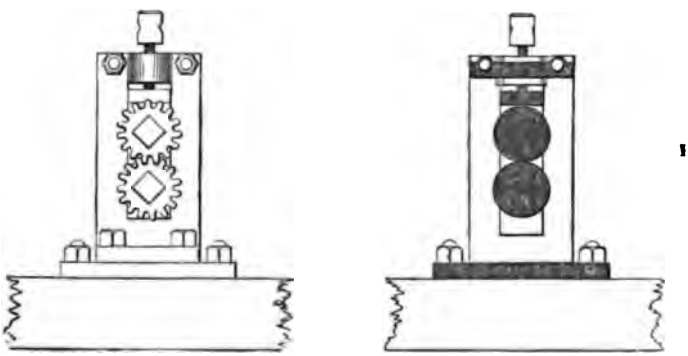
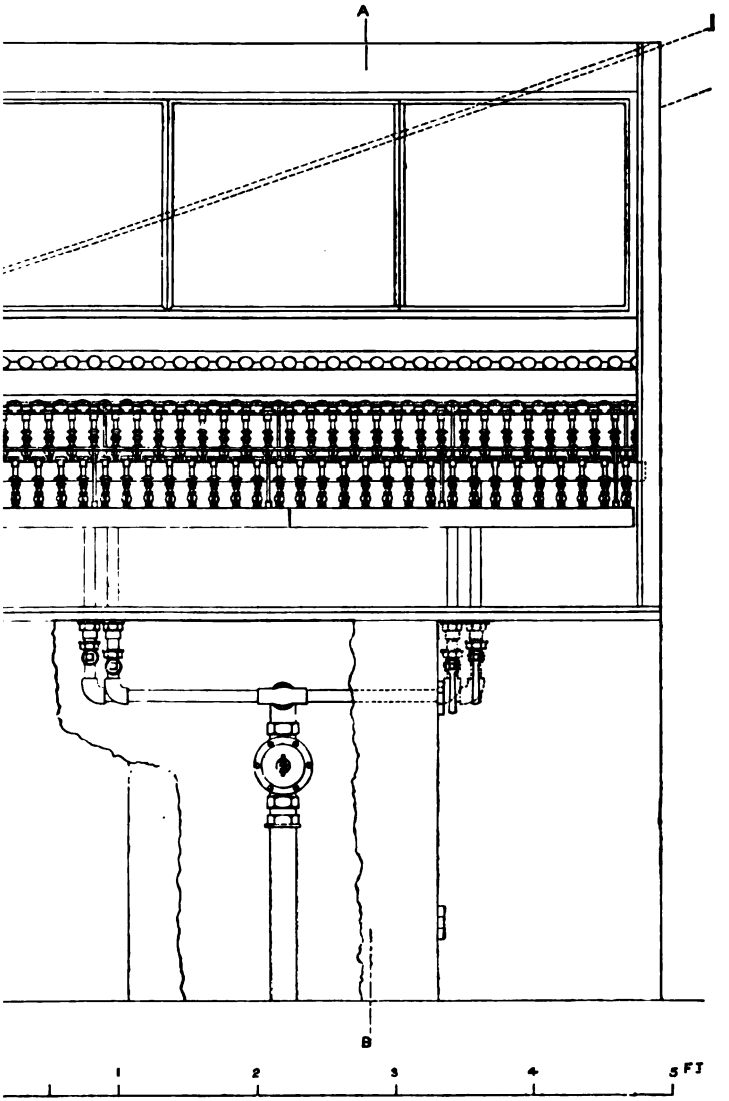


Fig. 34. End elevation on the gearing side.

Figs. 31–35. Rolling mill. The mill here represented is of the simplest and cheapest construction, and i required for common use by the assayer. But more costly mills may be procured in which the ro accurately adjusted by one motion.

TING APPARATUS.—The "parting" operation, to be subsequently
ed, in which the "cornets" are treated with boiling nitric
ay be conducted either in pear-shaped glass flasks or in pla-
ups in a platinum boiler.



Arrangement for two rows of air-gas burners for heating parting-flasks, shown in front
tion. The whole is contained within a glazed case, with windows in front which slide
ed down. The upper part of the case is connected with a chimney for exhausting the
s. From left to right is a sloping roof of slate or plate-glass, indicated by the dotted
by which arrangement the fumes are guided to the outlet.

KS.—When flasks are employed, a series, of which two are
ted in the section, fig. 37, is so arranged over a number of

rose air-gas burners (fig. 38), that several can be heated simul
ously. Each flask has a number engraved on its neck by wh
may be identified. The top of the burner is made slightly co
(see fig. 38), so as to keep the bottom of the flask in the centre

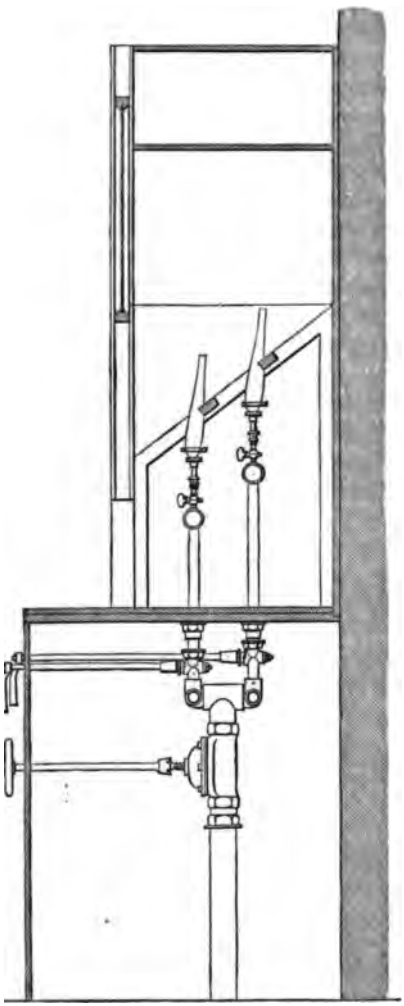


Fig. 37. The same arrangement as in fig. 36, shown in section.

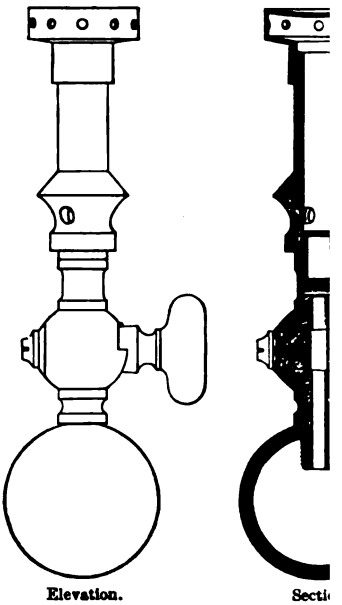


Fig. 38. Air-gas burner. Scale, half full size.

gas-jets; and in order to prevent the flask from accidentally sli
off, there is a fixed ring a little above the top of the burner.

PLATINUM CUPS AND BOILERS.—In 1854 Messrs. Henry and To
proposed to treat several cornets simultaneously by immers

[4] Journ. Chem. Soc. 1870. 23. p. 366.

number of glass tubes, perforated at the bottom, in a vessel of boiling nitric acid: such tubes are shown at G, H, I, fig. 39, but not to scale. H is simply a glass tube, like a common test tube, having several small holes in the bottom. I is a glass tube, closed at the bottom with a disk of platinum foil with numerous small holes in it. G is a glass tube, open at the mouth, but having a similar disk of platinum as in I, fixed a little above the bottom, which is open. Platinum, as every practical chemist knows, adheres firmly to glass heated to about the melting-point of the latter, so that such tubes as G and I may be easily prepared. It is obvious that by means of these tubes labour may be saved, as the trouble of pouring nitric acid into each parting vessel is avoided, and the process of washing the residue of gold is much facilitated and shortened; all that is needed being to dip the tube, with the bottom downwards, in successive portions of distilled water.

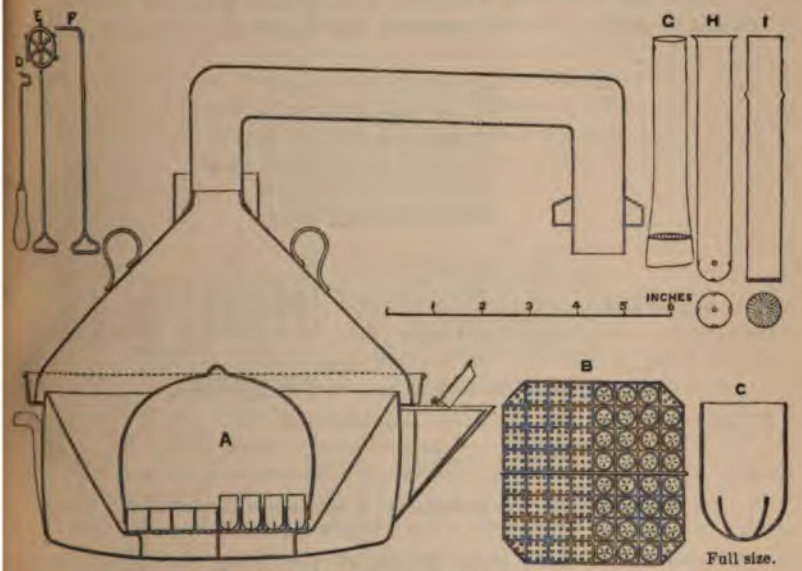


Fig. 39. A, vertical section of platinum boiler, containing the tray half charged with platinum cups. B, plan of the tray half charged with platinum cups. C, platinum cup of the full size. D, platinum hook for lifting the tray by the handle out of the boiler; not to scale. E, rotating peel for supporting the tray with cups during the process of annealing, not to scale; it should be about 3 ft. long. F, rod of iron bent at the end, to pull round the rotating part of the peel in the process of annealing; not to scale. G, H, I, parting tubes above described.

Messrs. Johnson, Matthey, and Co. substituted short platinum tubes, or thimble-like cups, for the tubes above described: a cup of this kind, of the full size, is shown at C, fig. 39; at the bottom there are five slits, which are fine enough to prevent any gold from escaping, and large enough to allow of the free passage of nitric acid or water. Two or three of these cups may be provided with wire handles for conveniently lifting them out during the process, in order to inspect the state of the cornet; in such cups trial-pieces, of exact composition, are placed, for checking the results. A considerable

number of cups are placed in a platinum tray, which consists of a bottom of sheet platinum, having numerous holes in it, and a framework of platinum wire in the form of trellis-work, dividing it into a number of equal square compartments. Such a tray is shown at B, fig. 39, in plan, and at A, fig. 39, in section, with half of the compartments empty and half containing their cups. It is provided with a fixed handle of strong platinum wire. The trays are now usually made circular, and not rectangular, like that in the preceding woodcuts. The tray, with its cups, is immersed in boiling nitric acid in a circular boiler of platinum, A, fig. 39; it rests upon a framework of platinum wire, which is kept in its central position by four pieces of platinum wire, inclining upwards and outwards and fixed to the edge of the boiler; two of these pieces are shown in A, one on each side of the handle of the tray. A hook of platinum is used for lifting the tray out of the hot acid by the handle; such a hook is shown at D, fig. 39, but not to scale. To the outside of the boiler are soldered at equal

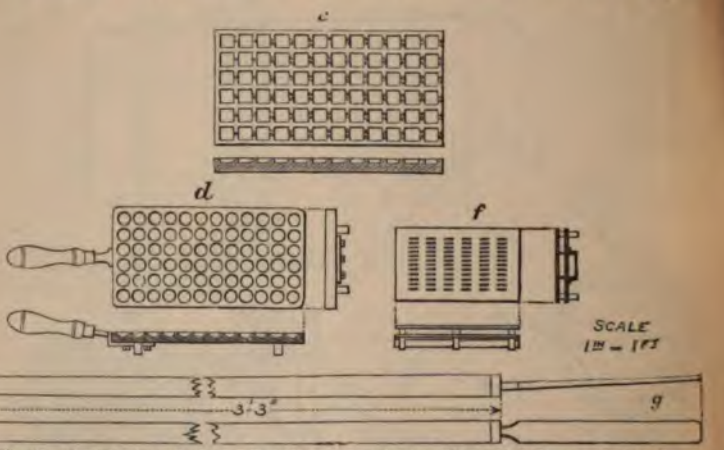


Fig. 40. *c*, wooden tray for lead-foil packets. *d*, metal-tray for assay-buttons. *f*, annealing iron for heating fillets. *g*, iron tool for introducing *f* into the muffle.

distances apart three stout pieces of platinum, or "lugs," one of which is shown on the left of the boiler. In the woodcut the horizontal line, representing the edge of the boiler, has been accidentally omitted under the top of the handle of the tray, above the letter A. The boiler is fitted with a hood of platinum, the lower edge of which drops into a channel extending round the upper edge of the boiler and kept filled with water. The top of the hood is connected by means of platinum tubes with any suitable arrangement for removing the fumes and condensing nitric acid. The boiler was formerly provided with a spout for pouring out the nitric acid, but in those recently manufactured by Messrs. Johnson, Matthey, and Co., and such as they themselves use, the spout is dispensed with. In the preceding woodcut, A, fig. 39, the boiler is represented with a spout, formed of two pieces of sheet platinum, which are a little distance apart at the top, but approximate downwards, and finally

touch each other, thus leaving a space between them, which is filled with water, and into which there dips a hinged cover. The boilers now supplied by the firm above mentioned are fitted near the top on each side with a small platinum handle, which passes through a tube of wood or glass in order that the boiler may be held without burning the fingers.

TRAYS.—Several forms are employed to keep the assay-pieces and the buttons produced in cupellation in order through the various operations. The tray shown at *c*, fig. 40, is of wood, and those at *d* and *f* are of iron. Their uses will be described as the details of the process are given.

Fig. 41. Bullet tray. The tray has a rim of about $\frac{1}{4}$ inch high: it is fixed on an iron tripod, each leg of which is inserted in a large leaden bullet with a view to stability. The height of the stem should be such as to bring the tray on a level with the floor of the muffle. The woodcut is to the scale of $\frac{1}{10}$th.

The little tray, shown in fig. 41, is intended for saving time in charging when lead bullets are used. It is best made of sheet-copper. The lead bullets may be conveniently placed on it before charging into the muffle.

SHEARS AND FILES.—Strong metal shears with blades about $1\frac{3}{4}$ inch in length are employed in cutting off the portion of metal for assay, and, in some offices, the adjustment of its weight is completed by means of a fine file, which is fixed on a tray in front of the assayer's balance.

GOLD-BULLION ASSAY.

The method universally adopted of assaying gold by cupellation and parting depends upon the facts, that fluid oxide of lead will remove certain oxidizable metals from the precious metals when in a fused condition, and that nitric acid will remove silver from alloys of gold and silver, without attacking the gold, when these metals are present in certain known proportions.

The system now practised by most assayers comprises six distinct operations, the details of which may be somewhat varied.

First Operation.—A properly taken sample of the metal to be assayed is flattened, and a clean portion is adjusted approximately by an assistant to an exact weight by cutting and filing, the assayer completing the adjustment on his more delicate balance. The weight taken varies with different operators, as already mentioned, from 5 to 16 grains. The $\frac{1}{2}$-gramme (7·716 grs.) pound is employed by French assayers, and where large numbers of assays are made of alloys of nearly the same composition the smaller pound may be recommended on account of the greater number of assay-pieces which can be introduced into the muffle at once, and the comparative ease with which the subsequent mechanical operations can be conducted: the larger weight is considered preferable when assays of alloys of very varied composition are performed simultaneously, as giving a more trustworthy sample of the metal under examination. At the Royal Mint the $\frac{1}{2}$-gramme and the 16-grain pounds are employed for the assay of coins and ingots respectively.

The assay-piece so prepared is now wrapped in a piece of lead-foil (formerly paper was employed) together with a certain amount of pure silver. The amount of silver varies slightly with different operators, but is generally about $2\frac{1}{2}$ times that of the gold assumed to be present in the assay-piece; care being taken that if the metal under examination contains silver, allowance be made in the calculation for the probable amount present, and that the silver added contains no gold. The amount of lead employed also depends upon the composition of the alloy to be assayed.

At the Royal Mint, in the case of standard gold, *i.e.* 916·6 per 1000 of alloy, the weight of lead employed is to the weight of alloy taken for assay as 8 : 1; or the ratio of the weight of lead to the weight of copper present is 100 : 1.

The lead-foil packet is placed in one of the numbered compartments of the wooden tray (*c*, fig. 40), its position being noted on the assay-paper. Assayers vary as to the manner in which the lead is added, some preferring to introduce lead bullets into the cupels and to charge the assay-pieces into the molten metal, while others put all the lead that is necessary in the wrapper of foil. In either case the total weight of lead must be constant for each quality of metal.

The formation of these packets completes the first operation.

Second Operation.—The floor of the muffle having been lightly covered with bone-ash, the requisite cupels are placed in position, and the muffle-front (*g*, fig. 24) is closed. When an ignited faggot has been placed on each side of the muffle and covered with charcoal, *c* is closed, the sliding doors *f f'* are brought closely together in front of the muffle, a sliding plate similar to *h* but without perforations is introduced, and the sliding doors *j j'*, *k k'* are opened. As soon as the charcoal is fairly ignited, anthracite is added, the supply being renewed at intervals of about a quarter of an hour. The muffle is usually ready for work in about an hour from the lighting of the furnace.

The packets of lead containing the silver and gold are now transferred to the cupels, arranged in rows corresponding to those on the tray, the muffle being at a bright orange-red heat. The assay-pieces are charged in over the top of the plumbago front (*g*, fig. 24), the object of which is to render the temperature of the muffle as equable as possible, and the slider *h* is placed in position. The air supplied to the muffle and furnace may be entirely regulated by the damper *b*.

The furnace operation should be performed rapidly, and so that all the cupellations may be completed at as nearly as possible the same time.

Distinct stages may be noted in the action which now takes place on the cupel. Almost immediately, the surface of the molten metal becomes covered with greasy-looking drops of litharge, which are rapidly absorbed by the porous cupel and replaced by others. They pass over the surface at first slowly, but as the operation continues move with greater rapidity. In from 8 to 20 minutes the metal suddenly appears uniformly dull and glowing, and iridescent bands, produced by extremely thin films of fluid litharge resulting from

the last traces of lead, immediately pass over it. On the disappearance of these coloured bands a bright liquid globule is left, and the peculiar action known as "brightening" occurs.

Although some assayers remove the buttons of metal from the furnace as soon as they are worked off, the practice cannot be recommended; for, in addition to the danger of upsetting a cupel, a button from an assay of nearly pure gold is in some danger of "spitting," though not to the same extent as in the case of silver. It is preferable, therefore, to close the muffle front (*g*, fig. 24) and keep open the furnace door *c* until the buttons have set: when this precaution is taken, the buttons are always found to be more malleable than when withdrawn in a liquid state.

The buttons (which are of the form represented at *a*, fig. 42) on cooling are removed from the cupels by a pair of sharp-nosed pliers, cleaned by means of a stiff brush, or by immersion in warm dilute hydrochloric acid,[5] and are usually introduced into the compartments corresponding to their cupels in the tray (*d*, fig. 40).

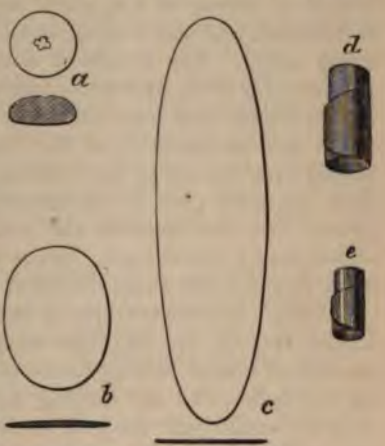


Fig. 42. Button, fillet, and cornet.

Third Operation.—The operation of "flatting," which now takes place, requires some skill, as on it, to a great extent, depends the accurate and regular formation of the "cornets" finally obtained. A hammer weighing about 7 lbs. (fig. 30) should be employed. The button is first struck directly in the centre: this blow should increase its diameter to about that of a sixpence when the ½-gramme pound is employed. It then receives a blow on the edge, so directed as to elongate the metal in one direction, and a similar blow is next given on the opposite edge, reducing it to the form shown at *b*, fig. 42. After annealing in the iron tray *f*, fig. 40 (which is introduced into the muffle by the tool *g*, fig. 40), or separately before the blow-pipe, the flattened buttons are passed in succession through the laminating rolls (figs. 31–35); and, after being reduced in thickness to about that of an ordinary visiting card, they are replaced in the tray *f*, and annealed at a dull red-heat. These "fillets" (*c*, fig. 42), as they are now called, can be easily bent by the finger into spirals or "cornets," as shown at *d* in the same figure, care being taken to form the coil so that the outer face is that which, before the flatting process, was in contact with the cupel, for a reason subsequently explained (see page 272). This face is easily recognized, as it is less brilliant than the other.

[5] C. Tookey, "On the Manipulation of Assays of Gold and Silver Bullion," Journ. Chem. Soc. 1870. 23. p. 367.

Fourth Operation.—In this operation, termed "parting," the silver, which was in the first process added to the assay-piece, in order to ensure the complete removal of any traces of this metal present in the alloy, is separated by solution in nitric acid, which must be free from chlorine, sulphuric and sulphurous acids. The cornets may be treated separately in the parting-flasks (fig. 37), or together in the platinum boilers, which have been already described.

The operation of boiling in flasks is conducted as follows:—From 2 to 3 fluid ounces (according to the assay-pound taken) of dilute nitric acid, the density of which is about 1·2, are poured into a flask of the capacity of about 6 ounces, and raised to the boiling-point. A cornet is then introduced and the boiling continued for about 8 minutes after the formation of nitric peroxide has ceased, when the flask is about two-thirds filled with hot distilled water and the fluid decanted. About 2 ounces of hot nitric acid of specific gravity 1·3 are now introduced, and the boiling continued for 15 minutes, when water is again added. The nitrate of silver solution is again poured off and the cornet washed by once or twice filling the vessel with hot distilled water, which is at once decanted. After the last filling, however, a small porous crucible, of the form shown at E, fig. 44 (p. 285), is placed over the top of the flask, and the latter is carefully inverted; thus the pure gold, in an extremely fragile and spongy state, falls gently into the crucible, the water which passes in with it being subsequently poured off. Great care must be taken to allow sufficient time for any small detached particles of gold to subside.

When a platinum boiler is used, the cornets having been arranged in the tray (B, fig. 39), the whole is introduced into the requisite amount of nearly boiling nitric acid, of specific gravity 1·2, contained in the boiler, and the boiling continued for about 15 or 20 minutes. It is important that the tray be not introduced until the acid is on the point of ebullition, as, when this precaution is not taken, the cornets are very liable to become blistered. At the conclusion of the operation the tray is immediately transferred to a second similar boiler, containing a somewhat less quantity of acid of density 1·3, previously raised to the boiling-point, and in this the cornets remain for about the same period. After successive dippings of the tray and cups in hot distilled water, the cornets are ready for annealing.

Fifth Operation.—The small crucibles, into which the cornets were transferred from the flasks, having been dried, are introduced into the muffle; and the cornets, which were of a dull brown colour and very friable, are annealed at a bright red-heat, whereby they assume a pure gold-yellow colour, and diminish considerably in bulk, *i.e.* in about the proportion shown at *e*, fig. 42.

If the platinum boiler is employed, the tray containing all the cornets should be introduced into the muffle, and the annealing be carefully conducted at a somewhat lower temperature to avoid adhesion between the platinum and gold. The tray may be supported on a rotating iron "peel," such as is shown at E, fig. 39; and thus the temperature at which the cornets are annealed can be equalized by rotating the tray without withdrawing it from the muffle.

Sixth Operation.—This, the final operation, consists in weighing the finished cornets, and reporting the results. The "checks," subsequently described, not less than three in number, are first weighed, and the mean excess or deficiency in weight (usually excess) is applied as a correction to all the assay-pieces worked with them; care must also be taken to subtract or add the "weighing in" correction according as it has been positive or negative. The weight finally obtained gives the amount of pure gold in the portion of metal operated upon; and, as the weights employed bear the definite relations to the initial weight explained at page 253, the report is at once indicated by the marks on the weights without further calculation.

Remarks and further Details relating to the preceding Process.—In cases where only copper is present as an alloying metal, and extreme precision is not required, cupellation is alone necessary. Indeed, according to Pelouze and Fremy,[6] it sometimes furnishes results more precise than the cupellation of silver, because gold is less volatile than silver. They state that the results obtained are always trustworthy to within 3-thousandths of the weight of metal operated upon; but the principal difficulty which the direct cupellation of such an alloy presents, consists in the fact that some gold is absorbed by the cupel when the temperature is high, and that it is impossible completely to remove the copper and lead when the temperature is low.

Preliminary assay.—When the composition of an alloy is unknown, it is essential that a preliminary assay be made, in order that in the actual assay the amount of gold, silver, and lead present may bear certain definite relations to each other. This determination may be made either by the touchstone or by cupellation; a skilled operator, however, can frequently judge with sufficient accuracy from the hardness and appearance of the alloy. Good preliminary results are obtained by cupelling 2 grains of the alloy with 6 grains of silver and 30 grains of lead; the button obtained is flattened and boiled with about half an ounce of nitric acid (free from chlorine), washed, ignited, and weighed. If silver is not likely to be present in quantity, the simple cupellation process above referred to will suffice.

Proportions of silver and lead required for cupellation.—Two circumstances must be considered in deciding upon the amount of silver to be added. On the one hand, after the removal of the silver the gold must not be left so spongy as to fall to pieces, and, on the other, it must be sufficiently porous to ensure the complete removal of the silver. Formerly assayers preferred that the metals should be present in the proportion of 1 of gold to 3 of silver, but both Chaudet and Kandelhardt recommend the proportion of 1 to $2\frac{1}{2}$; and it appears that more silver remains with the gold after the subsequent operation of boiling in nitric acid, when the larger proportion of this metal is added, than in the last instance. According to Pettenkofer,[7] the

[6] Traité de Chimie, 3. p. 128, 3rd edition.
[7] Bergwerksfreund, 1849. 12. p. 6.

separation of the two metals may be effected successfully when the gold and silver are present in the proportion of 1 to 1·75, provided that concentrated nitric acid be employed and that the boiling be sufficiently prolonged.

The amount of lead employed in the operation also depends upon the composition of the alloy, and authorities are as much divided on this point as on that just considered. The proportions recommended by D'Arcet[8] and Kandelhardt.[9] respectively, are given in the following tables, the ratio between the lead and the amount of copper present being also added:—

D'Arcet.			Kandelhardt.		
Approximate assay. Gold in 1000 parts.	Ratio of weight of lead to weight of assay.	Ratio of weight of lead to weight of copper present.	Approximate assay. Gold in 1000 parts.	Ratio of weight of lead to weight of assay.	Ratio of weight of lead to weight of copper present.
1000	1 : 1	——	1000	8 : 1	——
900	10 : 1	100·0 : 1	980 to 920	12 : 1	600 : 1
800	16 : 1	80·0 : 1			150 : 1
700	22 : 1	73·3 : 1	920 to 875	16 : 1	200 : 1
600	24 : 1	60·0 : 1			128 : 1
500	26 : 1	52·6 : 1	875 to 750	20 : 1	160 : 1
400		56·6 : 1			80 : 1
300	34 : 1	48·6 : 1	750 to 600	24 : 1	96 : 1
200		42·5 : 1			60 : 1
100		37·8 : 1	600 to 350	28 : 1	70 : 1
50		35·6 : 1			43 : 1
			350 to 0	32 : 1	49 : 1
					32 : 1

It will be noticed that, for the richer class of alloys, the amount of lead employed by the French assayer is considerably less than that recommended by the German.

[*Method of preparing the packets of silver, lead, and sample weighed for assay, at the Melbourne Mint.*—Mr. G. Foord has informed me (1873) that, in the assay department of the Melbourne Mint, the pure silver used in this process is cast into bars, which are rolled, and then cut in a fly-press into circular disks or blanks, 0·35 inch in diameter; the thinness to which the bars are rolled determining the weight of the disks. He also states that the lead employed is cast into bullets, flattened, and rolled into disks; and that these disks are folded upon a stick so as to form cases of definite weight and dimensions: these leaden cases, each charged with two silver disks, are arranged in boxes placed in a convenient position at the side of the assay-balance, and ready to receive the weighed samples.]

Temperature for cupellation.—The exact temperature suitable for cupellation can only be ascertained by practice, and the varying light of the day may occasion error in judging of the degree of heat, but it may be well to give a few general rules.

[8] Th. Bodemann's Anleitung zur berg- und hüttenmännischen Probierkunst. 2nd ed. 1856. p. 360. I cannot ascertain where D'Arcet's table was originally published.—[J. P.]

[9] Gold-Probirverfahren. Regulations for the Berlin Mint, p. 3.

The temperature is properly adjusted when the muffle is at a bright orange-red heat, the cupels of a bright red colour, the fused metal very luminous, and the lead fumes are seen rising slowly to the top of the muffle, and no crystals of litharge are formed on the cupel.

When the temperature is too high, the outline of the cupels becomes indistinct, the fused metal is seen with difficulty, and the fumes are almost invisible; and when it is too low, the fumes do not reach the top of the muffle, and a ring of indistinct crystals of oxide of lead forms on the top and outer surface of the cupel. Great care should be taken to ensure that the heat is so high before "charging in" that the chilling which necessarily takes place during this operation shall not cool the muffle below the requisite temperature. When charcoal is placed at the mouth of the muffle to prevent loss of heat, all carbonaceous matter must be carefully removed from the interior of the muffle, as this would have a prejudicial effect in reducing some of the litharge formed to the metallic state.

Indications of the presence of various metals afforded by the cupel.—As already stated, one end in view during the operation of cupellation is the removal by means of lead of all the oxidizable metals present, the precious metals being left in a nearly pure state on the cupel. But another and even more important point is attained; namely, the formation of a uniform alloy of silver and gold. When metals are present the oxides of which dissolve only sparingly in molten litharge—such as tin, zinc, nickel, and iron—they should be previously removed by scorification. The appearance of the cupel will frequently indicate the presence of these or other metals in the manner shown in the following table; but it should be added that the appearance due to one metal is so often masked by the presence of another that the indications given cannot be considered to be of much practical value:—

Metal.	Appearance of cupel.
Antimony	Pale yellow to brownish-red scoria, which sometimes cracks the cupel.
Arsenic	White or pale yellow scoria.
Chromium	Dark brick-red stain.
Cobalt	Dark green scoria and greenish stain.
Copper	Dark brown or green colour.
Iron	Dark red-brown stain at commencement of operation, leaving a dark ring on the cupel, which is corroded.
Lead	Straw or orange-yellow colour.
Manganese	Dark bluish-black stain and corrosion of the cupel.
Nickel	Dark green scoria and greenish stain.
Palladium, Platinum	Greenish stain and very crystalline buttons.
Tin	Forms a grey scoria.
Zinc	Yellow ring on cupel; the metal burns with a brilliant flame, gives out copious vapours, and corrodes the cupel.

Effect of the presence of platinum, palladium, iridium, and rhodium.—It is found necessary to conduct the cupellation at a higher tempera-

ture, and the iridescent bands remain longer, but are not so numerous. The surface of the button is dull after the operation has terminated, and is crystalline even when very small quantities of platinum are present. The presence of platinum and palladium is shown in the subsequent operation of parting, as well as by the appearance of the button.

Iridium, if present, being very dense, always sinks to the lower surface of the button while in a fluid state. Hence, when it is rolled into a cornet with the lower surface outwards, as directed at page 267, the least trace of this impurity, which shows itself as a black spot or streak, will at once be detected on careful examination.

The presence of platinum, iridium, and rhodium is very prejudical in the fourth operation, as they remain undissolved and render the assay unreliable; and further, the presence of platinum hinders the complete solution of silver.

Retention of silver in the gold obtained by parting.—It should be noticed that the silver present is rarely, if ever, entirely removed in the process of boiling in nitric acid; and Chaudet recommends an additional boiling in the stronger acid, after which he considers the metal to be pure. A more trustworthy practice, however, is to assay "check" pieces of pure gold side by side with the metal under examination, and to assume that the mean gain or loss of weight is the same as that experienced by all the assays worked with them. This subject will be more fully treated of in the sequel under the head of Checks or Standards.

Comparative advantages of platinum boilers and parting-flasks.—The use of platinum boilers is preferable where the amount of silver present bears such a relation to the gold that no cornet is in danger of falling to pieces; and further, the operation is less tedious, does not require so much skill, and the treatment to which the cornets are subjected is more uniform. Less acid is needed than when flasks are used, and in the Royal Mint as many as 144 cornets (of the ½-gramme assay-pound) are boiled in 100 ounces of acid. The method is specially useful on account of the great saving of time which it effects, where large numbers of assays are made of alloys of approximately known composition. The only objections to their use are the impossibility of detecting in any individual cornet the presence of such metals as plantinum and palladium, which impart a straw-yellow and deep orange colour respectively to the acid, and the liability of particles of gold to adhere to the platinum cups during the annealing process which subsequently takes place. This latter danger is, however, entirely avoided by annealing at a moderately low temperature. On the other hand, when flasks are employed, it is almost impossible to ensure that all the cornets are subjected to absolutely the same treatment during the process of boiling. Kandelhardt[1] proposes that all the cornets should be boiled in the same acid, after a number has been impressed on each by a punch to identify it, and this method is also recommended by Professor Stanley Jevons.

[1] Gold-Probirverfahren, p. 4.

[*Parting apparatus in use at the Melbourne Mint.*—The following information has been communicated to me by Mr. G. Foord:—At the Melbourne Mint platinum boilers are generally used; the old method of boiling in flasks being scarcely ever resorted to. For a smaller number of gold-assays, a modification of apparatus for boiling the cornets, proposed by Mr. F. B. Miller, has been adopted. The boiling vessel is an ordinary hard-glass beaker; and the cornets are arranged on pins of platinum wire projecting vertically from a horizontal frame or perforated plate of fine gold. In the case of a few gold-assays, a modification is employed intermediate between that proposed by Mr. Miller and the ordinary platinum boiler. A platinum tray with thimble-like cups is substituted for the frame with pins; and a beaker with etched graduations is employed as the boiling vessel: the tray has a handle, also of platinum wire, by which it is immersed and lifted out of the acid. This modification possesses the general convenience and economy of Mr. Miller's plan, while the advantages of boiling in cups are preserved, particularly that of altogether avoiding the use of forceps, etc., for removing the cornet.]

Retention of gas by the cornet.—Varrentrapp has pointed out that cornets are not strongly heated they remain porous and retain gas; and Graham [2] proved that, even after annealing, the weight of a gold cornet is increased about 2 parts in 10,000 by the occluded gas. This, however, does not invalidate the accuracy of gold assays, which are always made in comparison with pure gold as a check.

Checks or Standards.—The accuracy of the result of an assay is liable to be diminished either by a retention of silver or copper, or by an actual loss of a small quantity of the precious metal during the process, by sinking into the cupel, volatilization, or solution in the nitric acid. The weight of gold, therefore, as indicated by the balance, does not represent the amount originally present in the portion of metal operated upon; and as the error may be positive or negative, and varies with the heat of the furnace, strength and purity of acid, etc., it is necessary, as already mentioned, to assay, side by side with the alloys under examination, check-pieces the composition of which is known. Their importance was partially recognized as early as the fourteenth century, when their use was first prescribed by law;[3] and the metals have usually been present in the same proportion as they should be in the coin or plate under examination. As, however, it is impossible to guarantee that a mass of alloyed metal shall have absolutely the same composition throughout, and as any error in the composition of these check-pieces will be reflected in the results of all the assays compared with them, it is preferable to use pieces of pure metal corresponding in weight to the amount which it is anticipated the alloys to be tested contain, a small amount of pure copper being always added to each check to make the assays absolutely comparable. Of course, in preparing the metal necessary for such standards, it is not possible to

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[2] Phil. Trans. 1866. p. 433.

[3] Roberts on "Trial Plates." Appendix to the Report of the Deputy-Master of the Mint for 1873. p. 38.

attain to absolute chemical purity, and the presence of traces of i purity in them causes the results of assays to indicate the presence an amount of pure gold in excess of that actually present in the me under examination; but as the converse can never be the case, that to say, as the gold cannot be more than pure, no danger can ar from this cause, and the error can be easily allowed for. The c rection to be applied to a gold assay will be readily understood fr the following formula:

Let 1000 represent the weight of alloy originally taken;

p the weight of the piece of gold finally obtained;

x the actual amount of gold in the alloy expressed thousandths;

a the weight of gold (almost absolutely pure) taken as a che which approximately equals x;

b the loss or gain in weight experienced by (a) during t process of assay, expressed in thousandths;

k the variation of the "check gold" from absolute purity, pressed in thousandths.

Then the actual amount of fine gold in the check-pi $= a\left(1 - \frac{k}{1000}\right)$, and x the corrected weight of the assay will

$$= p - \frac{ak}{1000} \pm b,$$

(b) being added or subtracted according as it is a loss or gain.

If (a) be assumed to be exactly equal to (x), this equation becon

$$x = \frac{p \pm b}{1 + \frac{k}{1000}}.$$

Example.—Let p = 917·1 thousandths.
a = 920·0 „
b = 0·3 „ *gain* in weight.
k = 0·1 „

Then, by the first formula,

$$x = 917{\cdot}1 - \frac{920 \times 0{\cdot}1}{1000} - 0{\cdot}3;$$

for, as (b) is a *gain* in weight, it must be deducted.

Hence $x = 917{\cdot}1 - 0{\cdot}092 - 0{\cdot}3$
$= 916{\cdot}708.$

And, by the second formula,

$$x = \frac{917{\cdot}1 - 0{\cdot}3}{1 + \frac{0{\cdot}1}{1000}}$$
$$= 916{\cdot}708.$$

These two results show, therefore, that although (a) does exactly equal (x), no sensible error is introduced.

Surcharge.—The error represented by (b) which may be elimin in the manner above described is called "surcharge," as the amo of silver retained is usually in excess of the gold lost during

process; indeed some assayers mistrust their work when the reverse is the case.

As above stated, it varies considerably with the heat of the furnace and other circumstances. The surcharge is moreover greatly influenced by the amount of copper present in the alloy under examination. Thus, in an alloy rich in gold which has required only a small quantity of lead for its cupellation, the surcharge is slight: when, however, a large quantity of copper is present in the alloy, it becomes negative in consequence of the absorption of gold by the cupel; and for alloys containing 60 or 70 per cent. of gold the surcharge is zero. The following table of the results of experiments on synthetic alloys of gold and copper is given by Pelouze and Fremy:[4]—

Actual standard of the alloy.	Weight of the resulting cornet.	Difference.
900	900·25	+ 0·25
800	800·50	+ 0·50
700	700·00	0·00
600	600·00	0·00
500	499·50	− 0·50
400	399·50	− 0·50
300	299·50	− 0·50
200	199·50	− 0·50
100	99·50	− 0·50

The following experiments have been made in the Laboratory of the Royal Mint, in order to gain some information as to the influence of the several processes on surcharge.

In each of 36 assays 7·074 grains or 916·7 parts of pure gold and 0·643 grains or 83·3 parts of copper were weighed and assayed with 19 grains of silver and 62 grains of lead; these proportions being selected as being the amounts present in assays made of coin or other metal of the standard employed in this country.

Twelve of these were cupelled in what a fireman would call a "dull" fire, twelve at the temperature usually employed in assaying gold, and a third series of twelve at a temperature which was somewhat higher. The three series were "parted" at the same time in the platinum boilers, and the cornets were weighed in the usual manner, the balance indicating that the first 12 had a mean "surcharge" of 0·05 per thousand, the second 12 had lost 0·1 per thousand, while those worked at the highest temperature weighed 0·37 thousandths less than the gold originally introduced into the furnace.

The twenty-four cornets of the first and second series were then re-assayed side by side with checks in order to ascertain, from the amount of gold present, how much silver each cornet contained in the place of gold lost during cupellation and parting. The results showed that the assay-pieces first mentioned must have lost 0·645 part of gold per thousand, while those of the second series (in which the tem-

[4] Traité de Chimie, 3me édition (1865), 3. p. 1230.

perature was higher) lost 0·723 part per thousand, the silver retained being also different in the two cases. This loss may appear to be considerable; but it is interesting to note that, in the case of the most carefully conducted silver-assay by cupellation, the loss of silver is at least twelve times as great.

A separate experiment proved that, after boiling in the first acid, the average amount of silver retained is about 2·5 parts per thousand, which is, therefore, approximately the amount removed by the stronger acid.

Rössler[5] has shown that the amount of gold lost in the cupellation process increases with the amount of lead used, and decreases as the amount of silver is increased,—facts which are quite in accordance with the results of experiments recently made in the Royal Mint. He also considers that in general the gold lost is greater in amount than the silver retained by the cornet.

[The following is in great measure a copy of a paper on "Surcharge of the Bullion Assay," read before the Royal Society of Victoria, in 1875, by Mr. Robert Barton, formerly a student of the Royal School of Mines:—

It is generally understood by assayers that the surcharge of the gold cornet does not exactly represent the residue of silver which the parting has failed to boil out, and that it is on the contrary a resultant error; in fact, the difference between this silver residue and the loss which the gold suffers by volatilization in the muffle and absorption by the cupel.

As these two opposite sources of error vary according to circumstances,—such as temperature of the muffle, porosity of the cupel, thickness of the ribbon forming the cornet, quantity of lead and proportion of silver employed, strength of acid, and time of the operations,—it becomes necessary to control the work by the use of "proof" assays of gold of known fineness, which, passed with the work under exactly the same conditions throughout, show what correction for "surcharge" is to be made in each case.

The more closely a routine is adhered to—the same from time to time in all its minor details of temperature, using cupels of the same make, acid from the same bulk, etc.—the more uniform will the surcharge remain from day to day. But even when this approximate uniformity is secured, there still remains an influencing cause the neglect of which will lead to reports of a comparatively inaccurate character: *the loss on the cupel depends upon the quantity of gold in the assay*, so that the surcharge will be greater in samples of gold of high fineness than in those of low fineness passed in the same fire and parted in the same acids.

The loss of gold may be so great as exactly to neutralize the excess weight due to silver left in the cornet, when a surcharge = 0 will result; or the loss by volatilization may exceed what is required for compensating the excess weight due to remaining silver, when the surcharge will be represented by a negative sign. Something must

[5] Dingl. Polytech. Journ. 206. p. 185.

n such instances be *added* to the weight of the cornet in order to epresent the exact fineness of the sample assayed.

In practice, the variation of surcharge with the varying fineness f the samples may be compensated by passing, in the same fire, roofs of fine gold of weights approximately corresponding to the esumed fineness of the several assay-pieces under trial, and cor-cting each of the latter by its corresponding proof: thus, gold 0·9 by the 9 grs. proof, gold of 0·7 by the 7 grs. proof, and so (supposing the assay-pound in these instances to be 10 grs.). it with rough gold especially, of which often a large range of ienesses is passed in one fire, it would be exceedingly laborious to ovide proofs for each variation; and for commercial (as distin-iished from purely experimental work) some kind of general rule compromise has to be made.

The following is the mean of the results obtained in four series of perimental trials illustrating the preceding remarks:—

Silver employed 2½ times the weight of the gold.
Lead „ 84 grains.

ll other conditions were the same throughout.

Fine Gold. Grains.		Surcharge. Mean of results.
10	.....	+0·0008 518
9	.....	+0·0005 695
8	.....	+0·0004 114
7	.....	+0·0002 631
6	.....	+0·0000 114
5	.....	−0·0001 346
4	.....	−0·0004 380
3	.....	−0·0006 050
2	.....	−0·0010 596
1	.....	−0·0012 329

According to the above results when, with a full assay-pound of ne gold, the surcharge equals + 0·00085, then—

With 8 grs. under the same influences the surcharge is reduced to one-half;
„ 7 „ „ „ „ one-quarter;
„ 6 „ „ „ „ zero;
„ 2·4 „ „ the "minusage" is nearly equal in amount to the "plusage" at 10.

Of course, by altering the weight of lead, or in any other manner odifying the ruling conditions, other figures would be obtained; t special experiment under any given routine would show the inter-lation existing between the surcharges for the several finenesses gold.

Half of these experiments were performed by Mr. Barton and half Mr. Foord, with a view as far as possible to avoid personal error.]

It will be observed that as copper was not present in these experi-ents, the results are not strictly applicable to assays of gold-bullion.

Concluding Observations on the Assay of Gold.—Individual coins ued from the Royal Mint seldom exhibit a greater divergence m the exact legal standard than $\frac{4}{10000}$ths; that is, $\frac{1}{5}$th of the emedy" or allowance which the law permits. The amount of gold tracted in the British colonies alone during the year 1875 may be

estimated at not less than £16,000,000; and as this metal, unless converted into coin, has to be assayed every time it changes hands, it will be evident that the importance of ascertaining what is the limit of precision in gold-assays can hardly be overrated. Some estimate of this importance may be gathered from the fact that a persistent error of $\frac{1}{10000}$th in the assay-reports on one million of bullion would represent a gain or loss of £100. With a vew to determine the limit of error in gold-assaying, the authorities of the Bank of England[6] caused twenty bars of gold to be assayed by six assayers; and it was found that, while the maximum differences between their results on the several ingots varied from $\frac{2}{10000}$ths to $\frac{1}{1000}$th, the greatest difference between any assay-report and the mean of all the reports on the same ingot varied from $\frac{11}{100000}$ to $\frac{11}{100000}$.

This experiment is, however, open to the objection that it was not made on synthetical standards, in the preparation of which the most scrupulous care had been taken to ensure homogeneity. It is probable also that, when widely-divergent results are obtained, the divergence is increased by impurity in the gold employed for "checks" by the assayer who furnishes the highest report, and that either the amount of impurity has not been ascertained and allowed for, or that it has altogether escaped detection. In conclusion, it may be well to quote the opinion of M. Stas on this question,[7] who thus writes:—"The analysis is accurate within the limits of ± 0·0001; so that the total error cannot exceed 0·0002, which I take as the limit of precision of a gold-assay by inquartation, which only yields exact results by making compensations for errors."[8]

[Roberts and Lockyer, it may here be stated, have made an interesting spectroscopic investigation of the alloys of gold and copper, and have satisfied themselves that it is possible to distinguish between alloys of these metals differing in proportion only by $\frac{1}{10000}$ part.—Phil. Trans. 1874. 164. p. 495.]

Estimation of Silver in Gold Alloys.—In determining the amount of silver present in association with gold, two or three essays for gold are made by parting in the usual way, and duplicate assay-pounds of the alloy are at the same time cupelled without the addition of silver, but with sufficient lead to remove, as far as practicable, all the metals which are believed to be present and are oxidizable under the circumstances. The difference in weight between the button so obtained and the amount of gold indicated by the ordinary assay gives the amount of silver present in the alloy. Or the buttons from which copper has been removed by cupellation may, after weighing, be again cupelled with the addition of lead and such an amount of

[6] Third Report of the Standards Commission, 1868. p. 14.

[7] In a letter to Mr. W. C. Roberts.

[8] The word "inquartation" is here used as synonymous with parting. But its original meaning is "an operation by which the quantity of one thing is made equal to a fourth part of another thing," as in the preparation of an alloy of gold and silver which is suitable for parting, and in which the gold forms one-fourth part of the alloy. The word "quartation" has the same meaning as "inquartation." The process "is preparatory to the parting; and even many authors extend this name to the operation of parting." Translation of Macquer's Dictionary of Chemistry. London, 1771. p. 601.

silver as will make the weight of silver present about 2½ times that of the gold. The button is then treated with acid in the ordinary way, and the weight of silver is at once ascertained by subtracting the weight of the cornet from that of the button. The operation requires much practice, and satisfactory results can only be obtained by the aid of numerous check-assays of alloys containing known amounts of gold and silver.

Estimation of Gold in Silver Alloys.—In order to estimate the gold contained in auriferous silver it is only necessary to dissolve the alloy in nitric acid, and to collect, ignite, and weigh the gold which is left as a dark powder.

PREPARATION OF PURE GOLD.

Perhaps the following method, which was that adopted for the manufacture of the pure gold Trial Plate now in the custody of the Warden of the Standards, is the best. Gold cornets, from the purest gold which can be obtained, are dissolved in nitro-hydrochloric acid, the excess of acid driven off, and alcohol and chloride of potassium added to precipitate traces of platinum. The chloride of gold is then dissolved in distilled water in the proportion of about half an ounce to a gallon, when the solution is allowed to stand for three weeks. The supernatant liquid is then carefully removed by means of a glass syphon (the short arm of which is bent up) from the deposited silver chloride, and oxalic acid in crystals added from time to time until the solution becomes colourless, the precipitation towards the end being aided by a gentle heat. The spongy gold so obtained is washed repeatedly with dilute hydrochloric acid, distilled water, ammonia-water, and again with distilled water, after which it is melted in a Picardy crucible with a little bisulphate of potash and borax, and poured into a stone mould. The Trial Plate prepared by this method weighed about 70 ounces and was of the average purity 999·96, absolute purity being represented by 1000. [Formic acid is an excellent precipitant of gold, and so I find to be a solution of chloride of sodium containly cuprous chloride dissolved.—J. P.]

Silver-Bullion Assay.

The assay of silver-bullion may either be performed by cupellation, as already described under the Second Operation in the Assay of Gold (see page 265), or the composition of an alloy may be exactly verified volumetrically by precipitating the silver from its solution in nitric acid. There are also other volumetrical methods which will be subsequently described.

Cupellation-Assay of Silver.

As the process of cupellation has been already described, it will be only necessary here to point out the manner in which the estimation of silver differs from that of gold, and the precautions which must be observed in conducting the operation.

The cupellation-assay of silver may be divided into three distin operations, namely—

(1.) The preparation of the assay-piece.
(2.) Elimination of impurities by cupellation.
(3.) Weighing the buttons and reporting the results.

First Operation.—A portion of the alloy is adjusted to an exac weight, usually about 12 grains, in the manner already describe under the assay of gold; but additional precautions are necessary t ensure that the assay-sample represents the mass from which it is taken; for, as has been previously stated, alloys of silver and copper are peculiarly liable to undergo liquation. The assay-piece is enclosed in an envelope of pure sheet-lead, the weight of which bears a definite ratio to that of the copper present. The lead should be at least six times the weight of the assay-piece, and should be increased in proportion to the amount of copper present: the exact proportions usually recommended are given at page 281.

The assay-pieces thus prepared are placed on the wooden tray *c*, fig. 40, from which they are transferred direct to the muffle.

Second Operation.—The assay-pieces are introduced into the cupels in the manner previously described at page 266, and the phenomena which subsequently take place are the same in the two cases. In cooling down the furnace prior to withdrawing the assay-buttons special care must be taken to avoid the admission of cold air into the muffle, as this would be followed by the "spitting" above referred to —an accident which, at the Royal Mint, is prevented by the old method of surrounding the closed door with glowing coals, and not opening it until the upper coals in the furnace are black. A good button or "prill" is bright, crystalline, and slightly depressed in the centre, and dull white on the under-surface. The presence even o a very minute quantity of copper renders it less globular.

After all the buttons are set, the cupels are withdrawn and th buttons cleaned with a stiff brush, or by treatment with hydrochlori acid, as suggested by Tookey.[1] It is a common practice to remov the buttons from the cupels, and give each button a blow on its sid in order to liberate the adherent bone-ash before it is brushed. Th buttons are now ready for the final operation of weighing.

Third Operation.—In ascertaining the absolute amount of pure met present in the alloy, the system of balance corrections described page 253 is employed, and the results are controlled by "check assays of pure silver, or of metal the standard of which is known.

Remarks and further Details relating to the preceding Pro cess.—*Preliminary assay.*—The amount of lead to be employed i the cupellation depends on the composition of the alloy under ex amination; it is obviously necessary therefore that this should pr viously be approximately determined. An experienced assayer wi frequently be able to decide this with sufficient accuracy from th colour and hardness of the metal; but, when necessary, a preliminar

[1] Journ. Chem. Soc. 1870. 23. p. 367.

assay may be made by cupelling 2 grains of the alloy with 30 grains of pure lead, and working the assay in the usual manner. Or the composition may be roughly ascertained by comparing the appearance of a streak made by the alloy on a touchstone with those of a series of "test needles," or by noting the amount of oxidation produced on a clean piece of the alloy when kept heated in a muffle for a given time. (See p. 157 *antea*.)

Proportion of lead required for cupellation.—The following table gives the proportion of lead prescribed by D'Arcet[2] as the result of his experiments :—

Approximate assay. Silver in 1000 parts.	Ratio of weight of lead to weight of assay.	Ratio of weight of lead to weight of copper present.
1000	0·3 : 1	—
950	3·0 : 1	60·0 : 1
900	7·0 : 1	70·0 : 1
800	10·0 : 1	50·0 : 1
700	12·0 : 1	40·0 : 1
600	14·0 : 1	35·0 : 1
500		32·0 or 34·0 : 1
400	16·0 : 1 or 17·0 : 1	26·6 or 28·3 : 1
300		22·8 or 24·3 : 1
200		20·0 or 21·2 1
100		17·7 or 18·8 : 1
Pure copper.		16·0 or 17·0 ; 1

According to Makins, an assayer of much experience, there are great difficulties in working even fine silver with less than three times its weight of lead, and he is of opinion that results obtained on alloys very rich in silver are unworthy of trust when a smaller quantity is used. He employs six times its weight for the assay of metal of the English standard (925 parts per thousand), and increases the proportion for coarser varieties; in the Royal Mint similar quantities are used.

Temperature for cupellation.—It may be well briefly to point out that the management of the furnace during a silver cupellation differs slightly from that already explained at page 266. This difference arises from the fact that any metals other than silver must be eliminated in the furnace, and not by a subsequent treatment with acid, as in the case of gold-assaying. The difference of manipulation is also in part due to the necessity for taking special precautions to avoid a loss of metal from the expulsion of oxygen which attends the rapid solidification of the silver buttons. The proper adjustment of the heat therefore and gradual cooling of the assays are of the first importance.

It is advisable to keep the temperature as low as possible, so as to reduce the volatilization of the precious metal, and its absorption by the cupel, to a minimum ; but, on the other hand, care must be taken to avoid all risk of the buttons setting before the oxidizable metals

[2] Ann. de Chim. et de Phys. 1816. 1. pp. 66–76.

have been removed. The heat should be so adjusted that only slight fumes are visible over the cupels, and the fused metal should be very luminous and clearly distinguishable from the cupel. With too low a temperature crystals of litharge collect round the button: with an excessive heat, the fumes rise rapidly to the crown of the muffle.

Checks or Standards.—Since the amount of silver lost is much greater than in the case of gold, and varies considerably throughout the muffle, it is necessary that the checks should be more numerous. In the Royal Mint there are 9 checks in a fire of 45 assay-pieces, or one in each row, and the correction to be applied to an individual assay-piece is deduced from the checks in its immediate neighbourhood. Considerable skill and judgment are necessary in applying such corrections to the weights obtained, as well as a thorough knowledge of the manner in which the temperature varies in the muffle.

The amount of this correction need not exceed 10 parts per thousand, and from experiments by Hambly[3] it appears that the loss of silver increases as the quantity of lead employed is increased. Thus, with 5 grs. of silver and 5 grs. of lead, the loss of silver is 5·5 parts per thousand; while, when this weight of silver is cupelled with 175 grains of lead, the loss becomes 18·8 parts. He also found that, if the quantities of silver and lead present be increased in the same proportions, the loss per thousand parts slightly decreases: thus the mean of four experiments gave—

With	10	grs. of lead	and	1	gr. of silver	a loss of	12·25	per thousand.
„	100	„	„	10	grs.	„	11·35	„
„	250	„	„	25	„	„	10·67	„

Wet-Assay of Silver.

Formerly considerable difficulty was experienced in conducting the process of cupellation so as to afford accurate and uniform results; and, consequently, the varying loss of metal, which was not compensated for by any complete system of checks, caused the reports to be persistently 4 or 5 parts per thousand lower than the actual composition of the alloys. When extreme accuracy was required, as in Mints, this and other grave defects did not escape Tillet,[4] who conducted a series of experiments extending from the year 1760 to 1763, with a view to ascertain what were the principal sources of error. In the year 1829 a commission was appointed by the French Government to examine into all questions relating to the assay of gold and silver, and Gay-Lussac, a member of that commission, remarked with reference to the cupellation method, "It cannot be denied that an operation, which at the most does not require more than fifteen minutes, is one of elegant simplicity; but, nevertheless, the results which it yields cannot be adopted with a blind confidence;" and he was led to devise a wet or volumetric method of assay. His

[3] Chem. Gaz. 1856. 14. pp. 185–6.
[4] Mém. de l'Acad. Roy. des Sciences, 1761, 1763, 1769.

tructions for conducting the process were published in 1832, under title "Instruction sur l'Essai des Matières d'Argent par la Voie nide," and published in the appendix to a report of a Select Com-tee of the House of Commons on the Royal Mint in 1837.

The wet-assay of silver may be conducted in either of the three owing ways:—

(1) By ascertaining the *volume* of a standard solution which is uired to precipitate the silver present.

(2) By determining the *weight* of a standard solution which is uired to precipitate the silver present.

(3) By precipitating the silver by an excess of hydrochloric and calculating the weight of metal from that of the chloride ined.

The first method was proposed by Gay-Lussac, and is in common the second method, also proposed by Gay-Lussac, is not in use; the third method has been adopted in the Indian mints.

VOLUMETRIC METHOD BY CHLORIDE OF SODIUM.

TANDARD SOLUTIONS AND APPARATUS EMPLOYED.—Three solutions equired, namely,

(1) A standard or normal solution of chloride of sodium or salt.
(2) A decimal solution of salt.
(3) A decimal solution of silver.

When large numbers of assays are made, it is convenient to pre- periodically a considerable bulk of the first and third of these ions, which should be preserved in well-closed vessels of stone- or glass.

(1) *Standard solution of salt.*—This is made by adding a given ht of thoroughly dried pure salt, or of a saturated solution of to the requisite bulk of water. To prepare pure chloride of um, a concentrated solution of the best table salt is treated with ution of caustic baryta in order to remove sulphuric acid and nesia; a slight excess of carbonate of soda is then added, the ion is warmed, and the precipitate allowed to subside. The d is evaporated, and the crystals which form are separated by a , washed with distilled water slightly, dried and heated to dull ess; when cold, they are ready for use, or may be preserved in a closed bottle.

A simple calculation shows that, taking 107·929 as the atomic ht of silver, and 35·457 as that of chlorine,[5] and 23 as that of um, the chlorine contained in 54·162 grammes of salt will exactly ipitate 100 grammes of silver. Suppose, therefore, that we have ssel capable of holding N litres of water; take $5{\cdot}4162 \times N$ mes of pure salt and dissolve it in N litres of distilled water: olution obtained will suffice for $10 \times N$ assays. It is hardly

[5] Stas, Sur les Lois des Proportions chimiques, 1865. pp. 210–212.

necessary to observe that great care must be taken to ensure c solution.

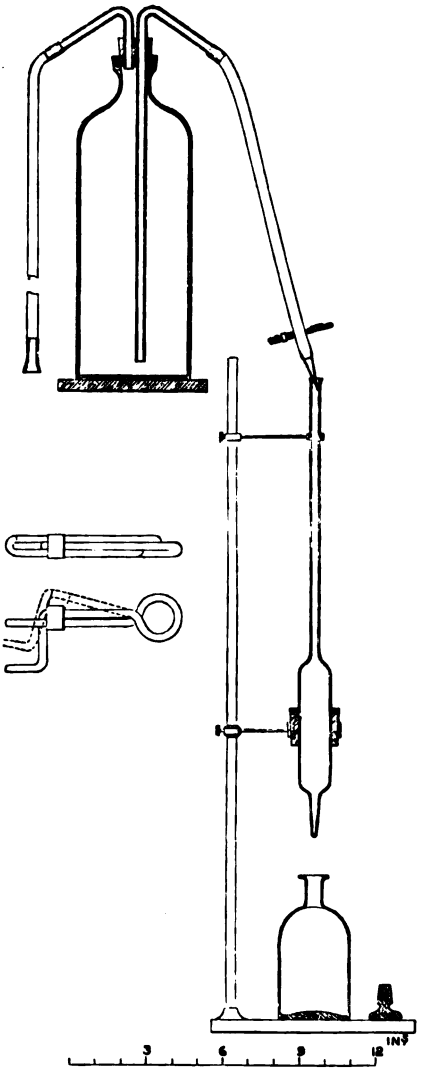
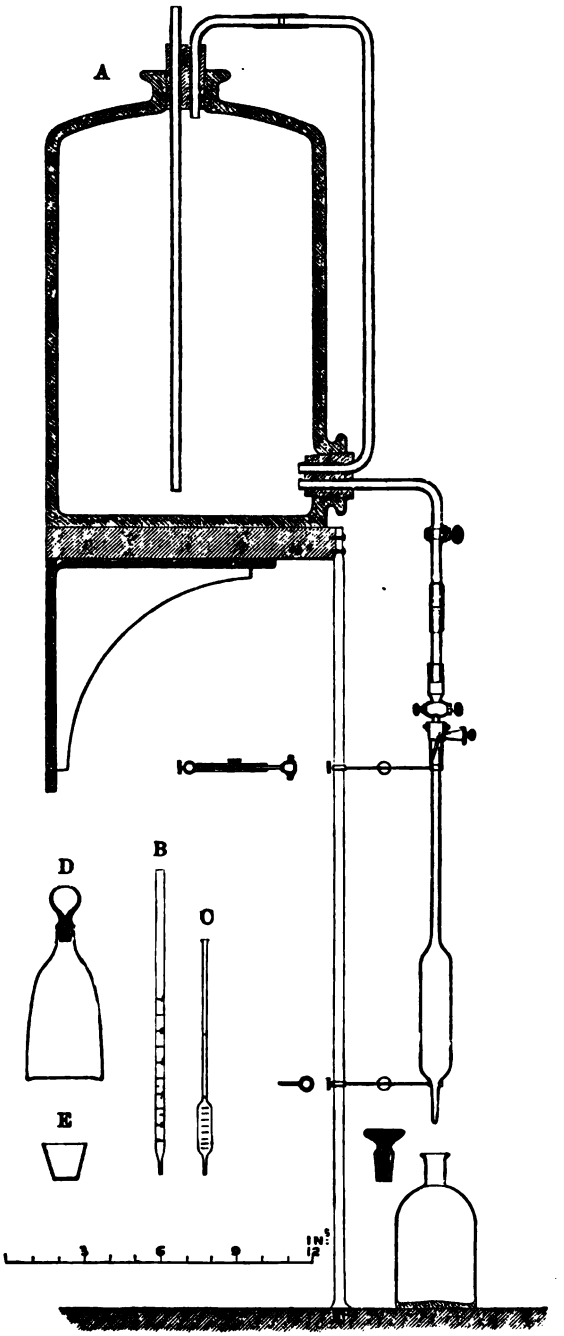


Fig. 43. Reservoir, 1000-grain pipette, and bottle, shown in vertical section. The clip for the india-rubber tubing is shown separately in plan and elevation on a larger scale.

When the second mentioned above is the quantity of saturat tion taken must be det by experiment, as it i to employ common wa to make allowance salt which it contain together with the sa solution added to it contain 5·4162 gram every litre of the The following quanti required when 20 gal normal solution are pr and from them some e may be made in othe Twenty gallons, or 90· will suffice for 908 since 100 c. c. are em in each assay. The of salt necessary, the is 908 × 0·54162, or 4 grammes; that is, Troy ounces. Such a qu is contained in 60 o of the solution, satur the ordinary temp (15° C.), allowance made for the small qu of salt known to be in the water which is in order to obtain the site degree of dilution. every gallon of norma tion should contain a mately 3 ounces of th rated solution of salt.

(2) *Decimal salt-s* —This is prepared by 9 parts of distilled wa volume, to 1 part of the above standard solution; and a con method is to introduce the contents of the 100 c. c. pipette, de below, into a litre flask and fill up with water.

[a] According to Mohr, a completely saturated solution contains 31·84% of salt, but the solution usually employed does not contain more than 26· the amount above given.



44.—A. Reservoir, 1000-grain pipette, and bottle. B and C. Two forms of 100-grain pipettes. D. and E. Bottle and cup used in the Indian Mint process.

neck, the adjustment necessary for different temperatures being given by a table. The external end of the movable tube is fitted with a glass cap having a fine opening, as in the Stas pipette. M. Sire also[1] employs a Mariotte-bottle as a reservoir for the salt-solution; and as the pipette is so arranged that its highest point is on a level with the lowest extremity of the vertical glass tube passing into the reservoir, the liquid will cease running at the moment the filling of the pipette is completed. The apparatus is thus to some extent self-acting, and does not require constant supervision, but the time occupied in filling the pipette is materially increased.

Decimal salt- and silver-solution pipette.—For the addition of decimal solutions of salt and silver a glass tube graduated in cubic centimetres is used. It is closed at the upper extremity by the finger, and the liquid is allowed to pass into the bottle through a small opening at the opposite end. For very delicate operations Mulder has devised[2] a dropping apparatus, consisting of a pear-shaped vessel fixed in a vertical position and filled with solution. It is provided with taps for regulating the flow, and the outlet is of such dimensions that 20 drops are equivalent to 1 c. c.

Agitator.—The shaking, always resorted to in order to induce the clearing of the solution, may be conducted by hand, two or four bottles being shaken at a time; but it more convenient to employ an agitator, fig. 46, which is usually capable of receiving ten bottles. The agitator consists of a central, hollow cylinder, to which externally are attached receptacles, *b*, for the bottles. The cover, *c c'*, when closed, retains the bottles in their places by means of springs shown at *d*. The apparatus is suspended by means of india-rubber springs, *f*, from a flexible arm, *e*, which is firmly fixed to a wall. A second spring, *g*, connects the agitator with the floor. An up-and-down motion is given to it by intermittently pressing it downwards with both hands.

Bottles.—Round bottles, capable of holding ten ounces, which as well as their stoppers are numbered, are usually employed; and the number on the bottle into which each assay-piece and the requisite quantity of nitric acid are introduced is noted on its assay-paper.

A shelf painted dead-black should be fixed in front of a window, which may be glazed with yellow glass, to receive the bottles during the addition of the decimal solution; it is provided with a blackened upright back 3·5 in. high, extending along its entire length, and the bottles are so arranged on it that the light passes through the upper part of the liquid they contain.

Water-bath.—A water-bath for heating the bottles is shown in fig. 47.

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[1] Annales de Chimie et de Physique, s. 4. 1873. 28. p. 108.

[2] De Essayeer-methode van het zilver scheikundig onderzocht; Utrecht, 1857. A translation of the first part of this work is given in vols. 4. (1861) and 5. (1862) of the Chemical News.

DESCRIPTION OF THE PROCESS.—The method is founded on the property which soluble chlorides possess of completely precipitating silver from its solution in nitric acid, without acting on any other metal with which it may be associated (except mercury, see page 290). Gay-Lussac prefers to use chloride of sodium, but hydrochloric acid or various other soluble chlorides may be employed. As the chloride of silver easily collects on shaking and leaves a clear supernatant liquid, the addition of a small quantity of either chloride of sodium or nitrate of silver will at once decide which is in excess.

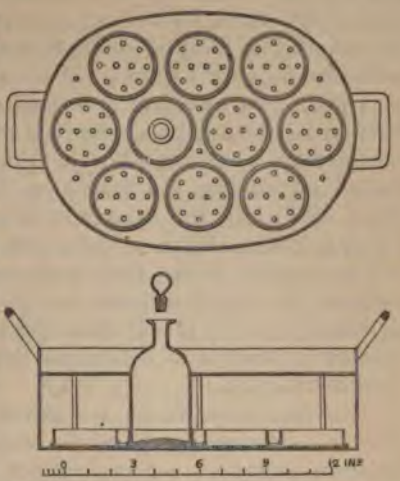

Fig. 47. Plan and vertical section of water-bath to hold ten bottles, with one bottle shown in position.

A portion of the silver alloy to be examined (the composition of which must be approximately known) is weighed, the weight taken being such that about 1 gramme of pure silver is present:[1] it is then dissolved in an ounce of nitric acid, of sp. gr. 1·190, by the aid of a gentle heat, and 100 c. c. of a standard solution of common salt are added, this standard solution being, as already explained, of such a strength that 100 c. c. will exactly precipitate 1 gramme of pure silver. The bottle now contains chloride of silver and nitrate of soda, and must be well shaken until the silver salt has curdled, leaving the liquid clear. It remains to be decided which is in excess, salt or silver. As two drops of the standard solution are sufficient to precipate 1 mgm. of fine silver, it would obviously be impossible in practice to ascertain the composition of an alloy by means of it within one-thousandth part. It is therefore usual to prepare a *decimal* solution of salt, one-tenth the strength of the standard or *normal* solution, so that 1000 c. c. will precipitate 1 gramme of silver. A drop of this decimal solution is now added to the contents of a bottle, and if a precipitate is formed 1 c. c. is introduced from a graduated pipette, and, after the bottle has been well shaken, another c. c., and so on as long as a precipitate is produced. If, on the other hand, the drop of salt produced no precipitate, showing that the pure silver present was less than 1 gramme, a

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[1] This amount is at once ascertained as follows:—

Let A be the composition as approximately known,

and x the amount of an alloy of this composition, which contains 1000 parts or 1 grm. of silver.

Then

$$A : 1000 :: 1000 : x,$$

$$\text{or } x = \frac{1{,}000{,}000}{A}$$

$$i.e. = \frac{1000}{A} \text{ grms.}$$

decimal solution of silver is used, prepared, as previously stated, by dissolving 1 gramme of pure silver in pure nitric acid and diluting to 1 litre: this solution is added in the same manner as the salt, until no further precipitate is formed. In either case the quantity of decimal solution is noted, and the results calculated in thousandths for 1 gramme of the alloy.

The method as above described suffices for determining the composition in thousandths, but it is possible by practice to attain to even greater accuracy. For it will be evident that the precipitate formed on adding the last c. c. of decimal solution might be so slight as to lead the assayer to believe that no precipitation would follow a fresh addition of salt; and further, as he knows the extent and appearance of the cloud produced when a full thousandth is precipitated, he might estimate by the eye the fractional part of one-thousandth, which is indicated by a less dense cloud. In this manner it is quite possible to determine the composition to within one ten-thousandth part.

Circumstances which influence the Accuracy of the above Method.—*Presence of mercury.*—As early as 1835[2] the divergence between assays on a certain ingot of silver led Gay-Lussac to the discovery, that the presence of minute traces of mercury causes the results of assays on silver to indicate an amount of precious metal in excess of that actually present; and this is the only metal which has since been found to interfere with his method. Although he was not successful in devising a means for avoiding this difficulty, he pointed out means for detecting mercury, even though only present to the extent of 1 part in 10,000 of the alloy. The circumstances to be noted are the following, to the first of which he attaches most importance:—

(1) The permanence of the white colour of the chloride of silver, even when exposed to a strong light; and

(2) The difficulty experienced in rendering the supernatant liquid clear by shaking.

As is well known, pure chloride of silver passes from a white to a blue colour with great rapidity when exposed to a strong light, and slowly in diffused daylight. If it contain 4 or more thousandths of mercury, it remains permanently white: with 2 or 3 thousandths the change of colour is very slight; with 1 thousandth it is well marked but still considerably less than in the case of pure metal; with half a thousandth the difference between the two is very slight. When the amount present is less than 1 thousandth, it can always be detected by the following simple artifice. One gramme or more of the metal is dissolved, and only sufficient salt added to precipitate, say, one-fourth of this amount. The mercury being first precipitated, is thus concentrated; and if only present to the extent of half a thousandth, and 1 gramme of the alloy has been taken, the precipitate will behave as though 2 thousandths had been present.

[2] Ann. de Chim. et de Phys. 1835. 58. pp. 218-224.

In 1846 Levol[3] suggested the following means of overcoming the difficulty. After the alloy has been dissolved in the ordinary manner, 25 c. c. of strong ammonia-water are added, and immediately afterwards 100 c. c. of normal salt solution. The excess of ammonia is then supersaturated with 20 c. c. of acetic acid, and the assay is concluded in the ordinary manner.

Gay-Lussac,[4] having confirmed Levol's results, suggested that acetate of soda should be substituted for ammonia and acetic acid, and this is a very convenient method in practice.

Debray[5] has studied the phenomena which take place in the above reactions, and shown the incorrectness of the explanation proposed by Levol, who considered that the double nitrate of protoxide of mercury and ammonia is endowed with a special stability, and that common salt in the presence of silver is incapable of acting on it. Debray finds that thoroughly washed chloride of silver placed in contact with perchloride of mercury changes its aspect, and whitens if partially discoloured from exposure to light. This is due to a partial reduction of the mercury salt to replace the chlorine lost by the silver. If a solution of nitrate of mercury is added to chloride of silver in suspension, the same effects are produced, and a certain quantity of silver is dissolved in the nitrate of mercury; but acetate of peroxide of mercury dissolves the silver salt with much greater difficulty.

The fact that a few thousandths of mercury in presence of alkaline acetates do not appreciably interfere with the accuracy of an assay can therefore be explained if it be admitted that an alkaline acetate has the effect of transforming the nitrates of silver and mercury into acetates, and alkaline nitrate being at the same time formed.

On this explanation, either the method of Levol or that of Gay-Lussac can be employed to restore an assay when the behaviour of the chloride has shown mercury to be present, and not solely that of Levol, as was formerly supposed. Debray has shown this to be the case. He points out that accurate results can be thus secured only when mercury is present in small quantity, and this fact as well as the difficulty in "clearing" when acetates are employed induces him to prefer a previous expulsion of the mercury by fusion for a quarter of an hour in the muffle in a small bone-ash crucible; and this practice he and Dumas have adopted in the Bureau de Garantie in Paris, without finding that the presence of volatile metals, such as zinc, causes any obstacle.

Mulder's neutral point.—Mulder has shown[6] that when the most exact chemical proportions of silver and salt are made to react on each other, the addition of either salt or silver to the clear supernatant liquid will produce a precipitate, indicating the presence of free nitrate of silver and chloride of sodium in a state of equilibrium, either of which is thrown down on the addition of the other, a

[3] Ann. de Chim. et de Phys. 1846. 16. pp. 504–7.
[4] Idem, 1846. 17. pp. 232–5.
[5] Comptes rendus, 1870. 70. p. 849.
[6] De Essayeer-methode vanhet zilver scheikundig onderzocht; Utrecht, 1857.

circumstance which was incidentally referred to by Gay-Lussac in his instructions published in 1832. Mulder considers that this peculiarity is owing to the presence of nitrate of soda, and has found that it varies with the temperature and the state of dilution of the liquid; but Stas has recently shown[7] that the alkaline nitrate is not the cause which determines the solution of the chloride. An example will make this phenomenon clear.

Suppose that in a given silver assay the decimal salt-solution has been added so long as a precipitate is produced, and that 1 c. c. of decimal silver is in turn required to precipitate the apparent excess: it would be found that when this had been done 1 c. c. more of salt solution would be wanted to reach the point at which no further cloudiness is produced. Mulder therefore recommends that only 0·5 c. c. of salt be added in this second case, and a point is thus attained at which salt and silver will produce an equal amount of precipitate. The solution now contains, according to his explanation chloride of silver dissolved in nitrate of soda, and the addition of either salt or silver expels it from solution.

A silver-assay may therefore be concluded in three ways:—

(1) By adding decimal salt-solution until it just ceases to produce a cloudiness.

(2) By adding a slight excess of salt and then decimal silver-solution until no more precipitate occurs.

(3) By finding the "neutral" point.

He considers the last to be the only correct method, and it preserves its accuracy at all temperatures up to 56° C. (133° F.), while the difference between the first and third methods amounts to 0·5 thousandth, and that between the first and second to 1 thousandth, at 16° C. (60° F.), and is sensibly increased by variation of temperature.

It is hardly necessary to add, however, that the first method is the most convenient in practice; and if care be taken that rather more than 1 gramme of silver is present, and one or more check-assays are performed from time to time, very great accuracy can be attained.

Method by Weight of the Chloride of Silver.

This method, consisting in the addition of an excess of hydrochloric acid to the solution of nitrate of silver, and in the determination of the amount of silver from the weight of chloride of silver obtained, was introduced by Dr. Dodd, Assay-Master of the Calcutta Mint in 1851. It is both convenient and exact.

The following brief description of the method of procedure is from a paper published by Dr. Busteed.[8]

After the samples for assay have been accurately adjusted, so that each weighs 18·817 grains (for a reason that will be presently given),

[7] Ann. de Chim. et de Phys. s. 5. 1874. 3. p. 177.

[8] Journ. Asiatic Soc. Bengal, 1870. vol. 39. pt. ii. No. iv.

they are transferred to specially-made 12-ounce glass bottles, one of which is shown at D, fig. 44, and each is dissolved by the aid of heat in 5·5 c. c. of nitric acid, of sp. gr. 1·200 for ordinary standard metal, or 1·320 for fine metal or when the nature of the alloy is uncertain. About 6 ounces of cold distilled water are then introduced into each bottle, and 5·5 c. c. of hydrochloric acid, of sp. gr. 1·060, are afterwards added. The bottles are allowed to stand for five minutes, and are then well shaken for three or four minutes till the chloride of silver aggregates and falls down. They are now nearly filled with distilled water, and allowed to rest for 4 hours. The supernatant liquid is carefully decanted by means of a syphon, and the chloride again washed with distilled water, gently shaken for a few minutes, and allowed to rest for two hours more. Under ordinary circumstances the chloride is now sufficiently washed, but if it is suspected to be "coarse" (*e.g.* to contain chloride of lead), one or two more washings may be given. The bottles are now placed in an inclined position in order that the chloride may collect into one spot. The chloride of silver is then transferred to a Wedgwood cup, shown at E, fig. 44, immersed in water, by inverting the bottle (with the finger placed over its mouth) and lowering it mouth downwards into the cup. Afterwards the chloride in the cup is broken up by means of a glass rod and dried, first in a steam-bath, and finally on a hot-air plate heated to 300° or 350° F., when it assumes the form of a cake, and may be easily transferred from the cup to the pan of the balance to be weighed while warm.

The weight of silver present can be deduced from that of its chloride, for every 100 parts of the latter contain 75·27 parts of pure silver; and 18·817 grains, the weight of metal taken, will therefore, if it be pure, yield 25 grains of chloride. Thus, if a decimal series of weights be prepared, in which the 1000 weighs 25 grains, they will, without calculation, indicate the standard of an alloy, provided that 18·817 grains were operated upon.

The silver is reduced and recovered from the chloride by fusion with chalk and charcoal.

Assay of Silver by Iodide of Potassium and Starch.

Pisani[9] has proposed a simple method of estimating the amount of silver present in a solution, based on the use of iodide of potassium and starch (see p. 165 antea). Field[1] has independently proposed the same method, slightly modified.

Vogel[2] subsequently proposed the following modification of the process:—On adding to a solution containing a silver salt, nitric acid charged with nitrous acid, iodide of potassium, and starch, two reactions take place. Iodide of silver is precipitated; and iodide of starch, which colours the liquid blue, is produced. So long as the least excess of silver remains undecomposed, this coloration disappears

[9] Ann. des Mines, 1856. 10. p. 83. [1] Chemical News, 1860. 2. p. 17.
[2] Pogg. Ann., 1865. 124. p. 347.

immediately on shaking; but if by a fresh addition of the iodide of potassium the point of saturation has been reached, a single drop of the reagent suffices to give a permanent blue colour to the entire solution.

The necessary solutions are thus prepared. Ten grammes of commercial iodide of potassium are dissolved in distilled water, so that the volume is 1023·4 c. c. One cubic centimetre of this solution will precipitate 0·01 gramme of silver. The nitric acid, containing nitrous acid, is prepared by adding 1 gramme of pure sulphate of protoxide of iron to 1000 grammes of nitric acid of sp. gr. 1·200; and a small quantity of the iron salt must be added from time to time. The starch is prepared as follows:—One part of starch is treated with 100 parts of warm water, the solution allowed to settle, and the clear liquid decanted: to this, 20 parts of pure nitrate of potash are added. The solution may be kept for about six weeks.

In making an assay by this method, 1 c. c. of the nitric acid is added to 1 c. c. of the solution under examination, then 10 or 12 drops of starch solution and a few drops of iodide of potassium. The addition of the iodide is carefully continued until a permanent blue coloration is produced, and the number of cubic centimetres added gives a direct measure of the number of centigrammes present.

The method yields good results in presence of acids and organic bodies, but is not applicable in presence of such bodies as salts of mercury, of protoxide of tin, arsenious acid, etc., which decompose iodide of starch, or of substances which colour the solution.

Estimation of Silver by Sulphocyanide (also termed Sulphocyanate) of Ammonium or Potassium.

Another volumetric method has been proposed by J. Volhard,[1] which is applicable in the presence of a considerable amount of copper. It is based on the fact that soluble sulphocyanides entirely precipitate silver, as sulphocyanide of silver, from its solution, and that this precipitate is unacted upon by mineral acids. By adding a solution of sulphocyanide of potassium or ammonium to an acid solution of a silver salt, containing a small quantity of sulphate of sesquioxide of iron, the whole of the silver is precipitated, while the small excess of the sulphocyanide solution gives a blood-red colour with the iron salt, and the end of the reaction is thus clearly defined.

As sulphocyanide of ammonium is too hygroscopic to be weighed directly, a standard solution is prepared as follows:—10 c. c. of solution of nitrate of silver, containing 10·8 grammes of pure silver per 1000 c. c., are introduced into a beaker, together with 5 c. c. of solution of sulphate of sesquioxide of iron (50 grammes to 1 litre of water), and a solution containing about 8 grammes of sulphocyanide of ammonium per litre is added until a permanent pale red tint

[1] Journ. für Chem. [2], 9. 217–222.

obtained. A hundred times the amount so required is diluted to litre, and each cubic centimetre of this solution is equivalent to) milligrammes of silver.

PREPARATION OF PURE SILVER.

The method usually employed for preparing the pure metal onsists in decomposing the chloride by galvanic action, and this is est done by enclosing a plate of zinc, into which a silver wire has een fixed, in a bladder or calico bag, and immersing the whole in he chloride of silver, covered with dilute sulphuric acid, care being aken that the wire passes into the chloride: the resulting finely-ivided silver is well washed, first with dilute acid and then with hot water, till all the acid and zinc salts are removed, and melted in the manner explained below.

The following method is recommended by M. Stas[4] [which, in my judgment, is not preferable to other, simpler, and perfectly satisfactory methods—J. P.]. It depends on the complete reduction which ammoniacal solutions of silver salts undergo when acted upon by ammoniacal sulphites of copper, or rather by a mixture of sulphite of ammonia and an ammoniacal salt of copper.

Standard silver is dissolved in dilute boiling nitric acid, and the solution of nitrates of silver and copper evaporated to dryness, the saline mass being then fused in order to destroy any nitrate of platinum that may be present.

On cooling, the nitrates are dissolved in excess of dilute ammonia, the solution being then allowed to stand for 48 hours, after which it is passed through a thick paper filter, distilled water being added until the weight of silver is not more than 2 per cent. of that of the whole bulk.

The requisite amount of sulphite of ammonia is thoroughly mixed with this argentiferous solution, and the whole allowed to stand for 48 hours in a closed vessel. At the end of this period, about a third of the silver present will have been reduced to the metallic state, in consequence of the cupric becoming a cuprous salt, the metal being deposited in the form of very brilliant greyish white crystals. By heating the supernatant liquid to a temperature of about 65° C. for some hours, nearly all the remaining silver is precipitated. The solution is now decanted, and the metal, obtained from the hot and cold solutions, separately washed by decantation with ammoniacal water until the washings cease to turn blue on exposure to the air and to precipitate chloride of barium. The silver is left for several days in strong ammonia-water, and, after thorough washing with distilled water, is melted with nitre and borax.

Mulder recommends that the melting be done in a porcelain crucible immersed in sand, contained in a common earthenware crucible; borax should be sprinkled over the sand, in order that when

[4] Sur les Lois des Proportions chimiques, 1865. p. 32.

the metal is poured no particles of dirt or sand may fall into it. The metal so obtained is either granulated or poured into a shallow mould formed by pressing a glass plate into a slab of soft pipeclay. The plate of silver is washed with boiling water to remove surface impurities, and rolled into thin strips.

NOTE.—*Estimation of Silver in Lead.*—Whether the estimation of a small quantity of silver in lead be made by scorification and subsequent cupellation, or by direct cupellation, the amount obtained in both cases is the same, as may be seen from the following results obtained by R. Smith from experiments with the *same* lead:—

I. 7000 grs. of lead scorified to 112 grs., and then cupelled, gave 0·127 gr. of silver, which is equal to 0·0181 per 1000.

II. 1800 grs. of lead scorified to 103 grs., and then cupelled, gave 0·032 gr. of silver, which is equal to 0·0178 per 1000.

III. 1000 grs. of lead cupelled gave 0·0180 gr. per 1000.

GAS-MUFFLE FURNACE.

The gas-muffle furnace which I have selected for description is the invention of Mr. Arnold T. Watson, and has been in use since 1867 at the Sheffield Assay Office, which is open for business on two days a week; and it is reported to have worked satisfactorily during the whole of that period. On applying to Mr. Watson for information on the subject, I received from him the following description, together with excellent drawings of the furnace, from which the woodcuts annexed have been copied. It should, however, be stated that this furnace differs in some of its details from the original one, though both are exactly alike in principle. When the furnace is quite cold an hour is required to heat it to the temperature suitable for assaying, but only about half an hour when it is warm, from having been in use a few hours previously.

When lighting the furnace, the air-valve (*c*), ventilators (*d d*), and chimney-damper (*e*) should be closed, and only gas admitted through the pipe (*b*). The gas, after passing through the fire-stone burner (*f*), is ignited through the opening (*g*). The ventilators and chimney-damper should now be quickly opened, and air gradually admitted into the mixing-chamber (*a*), by means of the valve (*c*), until the flame becomes blue, after which the opening (*g*) is closed with the fire-stone plug. This flame, which is smokeless, entirely envelopes the muffle (*h*) before passing away through the chimney (*k*). The draught, besides carrying off the products of combustion, converts each jet of gas, as it issues from the fire-stone burner, into a blow-pipe flame. This is in a measure effected by currents of air, which, being admitted through the ventilators, are drawn through the grooves in the surface of the burner between each series of jets. The heated chimney creates a

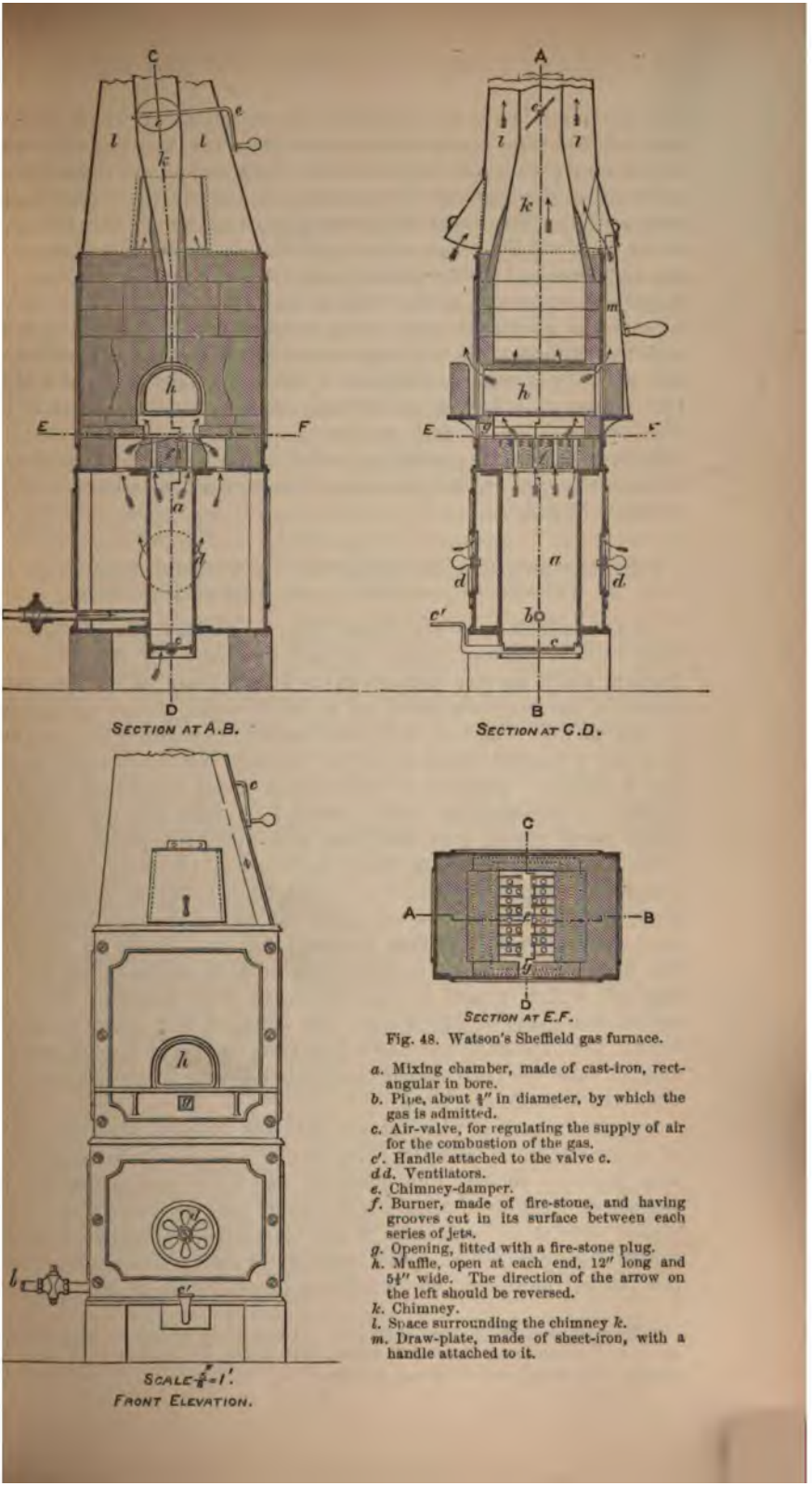

Fig. 48. Watson's Sheffield gas furnace.

a. Mixing chamber, made of cast-iron, rectangular in bore.
b. Pipe, about ¾″ in diameter, by which the gas is admitted.
c. Air-valve, for regulating the supply of air for the combustion of the gas.
c'. Handle attached to the valve *c*.
d d. Ventilators.
e. Chimney-damper.
f. Burner, made of fire-stone, and having grooves cut in its surface between each series of jets.
g. Opening, fitted with a fire-stone plug.
h. Muffle, open at each end, 12″ long and 5¼″ wide. The direction of the arrow on the left should be reversed.
k. Chimney.
l. Space surrounding the chimney *k*.
m. Draw-plate, made of sheet-iron, with a handle attached to it.

current of air inside the casement (*l*), by means of which fumes of oxide of lead from the muffle are conveyed away, through a hole made for that purpose in the flue above the furnace-chimney and within the casement. The current of air through the muffle is produced by means of the loose sheet-iron draw-plate (*m*), which can be applied so as to partially close either end of the muffle, the current from the opposite end being passed into the chimney casement. The improvement in the muffle consists in its being open at both ends, so that the assayer is enabled to watch the progress of the assays, and to regulate their working more effectually than is possible with the ordinary furnace. In such a muffle as that described thirty-two assays, of 1 dwt. of silver each, are frequently made at a time. The consumption of gas is from 80 to 100 cubic feet per hour. The furnace can be gradually cooled down by partially closing the chimney-damper, entirely shutting the air-valve (*c*), and reducing the quantity of gas.

CHINESE METHOD OF ASSAYING SILVER BULLION AND OF PREPARING "SYCEE"[5] OR UNCOINED SILVER.

I am indebted to my friend Mr. C. Tookey for the following account of a process which he saw practised by the Chinese at Canton, while he was assayer at the Hong Kong Mint. A circular vessel of earthenware, about 12 in. in diameter at the top and 9 in. at the bottom, and 5 in. deep, was coated internally with clay, so as to leave a central cavity 5 in. in diameter, which widened upwards like a funnel. The lower part of this cavity was filled with lime, slightly compressed, to within about 1 in. from the top. Sheets of paper were placed over the lime, and upon the paper 100 dollars (coined at the Hong Kong Mint) in two rows, together with an equal weight of lead. A cylinder of burnt clay, 11 in. in diameter, 3½ in. high, and ½ in. thick, was set upon the top of the clay lining of the earthenware vessel, and then a second similar cylinder on the top of the first. There was a notch at the bottom of the upper cylinder through which passed a pipe connected with bellows. This pipe, which was made of burnt clay, was straight, and closed at the end within the cylinders, but had a hole in it on the under side near the end, so that the blast might be directed downwards upon the metal. Charcoal was the fuel used.

Ignited charcoal was thrown into the furnace over the mixture of dollars and lead, and the blast let on; and as soon as the mixture was perfectly melted, the charcoal was raked and blown from the surface of the molten metal; after which long pieces of charcoal were placed over it on each side of the blast-pipe. Cupellation now followed, during which the blast was feebler than that used for effecting the fusion; and when the workman concluded from the appearance

[5] This word is the foreign rendering of the Chinese word "sai-sź," which means "fine silk," and evidently relates to the finely fibrous or silky fracture of fine silver.

of the metal that this part of the process had been continued long enough, all the charcoal was removed and water was sprinkled over the metal in order to solidify it. The cake of metal, which was as yet only partially refined, was detached and hammered on the floor of the workshop, which consisted of blocks of granite, with the view of separating from it as much adherent slag as practicable. The further purification of the metal was effected in another furnace, of which the bed sloped downwards and backwards, and the working part was open. A dried clay crucible was placed in the furnace and gradually heated, and at the same time the hammered cake of impure silver was placed upon the ignited charcoal. After this, the heated cake was put into the crucible; and when it was melted, an assistant dropped small pieces of nitre, from time to time, into the crucible, which was kept inclined towards the front of the furnace, with its mouth partially open, in order that he might be able to see into the interior and watch the action on the molten silver. The slag, resulting from this action, was removed by dipping in it a thick flat disc of iron, previously made hot, and scraping off what adhered to it, on the edge of a tray placed near for the purpose. As the silver became more and more free from alloy, portions of it were taken out, in a small red-hot crucible, and poured into an iron ingot-mould, in order that the workman might judge, from the appearance of the upper face of the ingot when cooled, whether he had brought the silver to the desired fineness; and if any crystalline structure was observed in the centre of that face, the ingot was put back into the crucible, and more nitre was added. The same treatment was repeated until an ingot or "shoe"[6] was obtained which presented a smooth non-crystalline surface throughout. When this occurred, the treatment with nitre was discontinued, and the whole of the silver was cast into lumps, each of the weight of 11 ounces troy; and such silver was valued as pure Hai Kwan[7] Sycee by the Chinese officials.

Mr. Tookey assayed two out of seven "shoes" which he saw thus cast, and found the standard of both to be the same, and only $\frac{986}{1000}$ fine, *i.e.* in 1000 parts of the silver there still remained 14 parts of alloy. Such a method of assaying silver bullion as the preceding, it need hardly be stated, would not be tolerated by European, American, or Australian bullion-dealers. Mr. Tookey remarks, that, "strictly speaking, it is a process of refining, but uncertain in its character, inasmuch as the operator depends entirely upon the appearance of the silver at what he considers to be the limit of purity, and because, as will be shown, he is ignorant of the fact that the alloy has not been completely removed at the end of the process." Now, it may be asked, what is the ordinary process of

[6] So called in English because, by a stretch of fancy, it has been likened to a shoe in form.

[7] The word means "Maritime Customs;" and "Hai Kwan Sycee" is the fine silver which is paid into the Hai Kwan Banks (the Banks of the Customs at Shanghai and other ports) for duties on silk, opium, tea, etc.

cupelling silver alloys but a method of refining by means of lead, and upon what does the assayer in this country rely as a sufficient indication of purity but the appearance of the silver? In the Chinese method nitre is the oxidizing agent, and a very powerful agent it is; while, in the other case, the agent is atmospheric oxygen. My conviction is, that by means of nitre it is possible to render silver finer than by means of lead. Lead, notwithstanding our pretended skill in silver refining, is, as has been previously shown in this volume, commonly present in our silver refined by cupellation, though in very small quantity it is true, and has been found in very appreciable quantity both in many European and American coins. As the Chinese have practised the metallurgic arts from remote antiquity, and must especially have had vast experience in the treatment of silver, it seems to me highly probable that an expert Chinese silver assayer would be able to form a pretty accurate opinion as to the purity of his silver. But the Chinese are reputed to be a cunning people, and, to use a somewhat vulgar expression, particularly wide awake in financial matters; and their dealers in silver know very well that if they could palm off impure silver for pure silver among their less knowing countrymen, it would be to their pecuniary advantage. There are men, even in this country, who would not be more scrupulous in that respect than the Chinese, so long as they believed that detection and punishment were not probable.

But to return to the subject. That the Chinese method of assaying silver bullion is open to many objections no one who has any knowledge of the metallurgy of silver can doubt. According to Mr. Tookey, the time spent in melting the dollars and lead together was unnecessarily long; the temperature produced by the blast was too high; during the second stage, the quantity of fume was excessive; and throughout the operation the conditions were such as to cause loss of silver. The Chinese, it is true, made an allowance for the loss of silver, but it was, as Mr. Tookey asserts, decidedly too small. They, however, did not take into account the error which might arise from the presence of silver in the lead which they used; and as the Chinese officials made no mention of silver in that lead, a portion of the same kind of lead was assayed, and found not to contain silver enough to affect the result, as it only amounted to 1·4 grain in the total quantity of lead used in the assay.

The weight of 100 Hong Kong dollars, by the Mint balance, was 86·65 troy ounces, or 41,592 grains (the standard weight of the dollar being 416·0 grains), and by the Chinese balance and weights, 71 taels 9 mace 2 candareens, or 41702·09 grains.[8] The weight of Hai Kwan Sycee, produced from 100 dollars, in the trial witnessed by Mr. Tookey, was 64 taels 3 mace 3 cand., or 37301·1 grains; and the weight of the silver computed to have been carried away by the lead was 0 tael

[8] The tael = 579·84 grains.
The mace = 57·98 „
The candareen = 5·79 „

4 mace 0 cand., or 231·93 grains, so that, taking the Chinese weights, we have $37301 \cdot 1 + 231 \cdot 93 = 37533 \cdot 0$, and $\frac{37533 \times 1000}{41702} = \frac{900}{1000}$, the standard fineness of the Hong Kong dollar. The Sycee, however, which, in the calculation by the Chinese, is considered as pure, contains only $\frac{986}{1000}$ of silver, so that the actual weight of silver in 37301·0 grains is 36778·88 grains; and adding the 231·94 grains allowed as compensation for loss, we have a total of 37010·81 grains; then subtracting this from the real amount of silver in the 100 dollars, there remain (37433 − 37010·81) 422·19 grains, the amount of loss unaccounted for.

It should be added that the trial above reported was made at Canton in order, if possible, to remove the prejudice on the part of the Chinese against the Hong Kong dollar; and fortunately with a successful result, as they agreed to accept that dollar at its real standard in payment for Customs' dues. But Mr. Tookey concludes by expressing his opinion that this result was due more to a fortunate accident than to the use of a correct method of valuation.

STATES IN WHICH SILVER IS IMPORTED INTO ENGLAND, AND THE NECESSITY OF PRECAUTIONS WITH RESPECT TO ITS PURCHASE.

I am indebted for the following important information on this subject to my friends Messrs. Johnson, Matthey, and Co., the well-known refiners of gold, silver, platinum, iridium, etc., in Hatton Garden, London.

Silver bullion arrives in this country from the American continent, North and South, in various forms. That from Nevada, California, etc., is in rectangular oblong bars of various sizes, which weigh from 1000 to 1500 ozs. each, and differ in content of silver from 100 to 999 per 1000, and which may or may not be free from gold. If "doré" (*i.e.* the term applied to such as contain gold), the proportion of gold seldom exceeds $\frac{1}{3}$ of the weight, the alloy or base metal present chiefly consisting of copper and lead. The weight, assay-produce, name of assayer, and value in dollars are usually stamped upon each bar.

The metal is sold in the state in which it arrives, unless of low quality, when it is usually remelted here by one of the Bank of England melters. A very large amount of silver comes from Mexico in the form of coined dollars, and is usually sold in that form for the China market, where the dollars are received as currency. Some Mexican dollars contain enough gold to pay for its extraction; and these are generally distinguishable by certain letters upon them, specifying the Mint in Mexico where they were coined, and they are assorted accordingly. "Plata Piña" is another form in which silver is imported into this country from Chile, Peru, and a few other localities; and such silver having been obtained by the process of amalgamation is generally in cylindrical or polygonal masses, accord-

ing to the form of the moulds in which the amalgam was pressed in order to expel the excess of mercury, the remaining mercury having been driven off by heating the resulting solid amalgam to redness, but not to the melting-point of silver. The "Plata Piña" sometimes contains gold, and is invariably melted previously to sale in this market, and in melting it there is always a loss varying from about 2 per cent. to 10 per cent., which is due partly to mercury and partly to sundry impurities, such as earthy matter and metallic oxides which the amalgam contained, and which were not removed in its subsequent treatment. After fusion, however, the metal is frequently 999 fine. It occasionally happens that pieces of iron are found floating on the surface of the molten metal, which had doubtless been inserted in the soft amalgam by roguish employés, who had stolen some of the amalgam and substituted an equal weight of iron. Cases have been known in which the percentage of iron, so imbedded, has exceeded half the total weight of the silver, the whole having been paid for by the West Coast houses as "Piña Silver." It seems strange that such a clumsy method of pilfering should have been successfully practised, as the fraud might immediately have been detected by cutting the piece of "Piña" in two.

Silver is also imported into this country from South America, in the state of coin, such as Sols, Bolivian dollars, etc.; but at present the chief import is in bars weighing from 2000 to 3000 ozs. each, the metal having been cast into such large masses with a view to reduce the chance of robbery. These bars are of various shapes, but most commonly are half-cylindrical (*i.e.* the half of a cylinder divided longitudinally), or rectangular, with a lip projecting from each end at the top. The former are generally of fine quality, ranging from 995 to 999; but the latter vary in fineness from 950 to 990, and are extremely *hard*. These hard bars contain a small proportion of sulphur, antimony, and arsenic, which, without rendering them absolutely brittle in many instances, has caused endless disputes, for the Mints will not accept metal so contaminated as "fit for coinage," or on a par with fine silver. Up to the end of 1875, these large bars were invariably melted upon arrival, as a necessary protection to the purchaser, and afterwards refined; but this is no longer done, and they are sold in the state in which they are received; so that with a view of saving the cost of remelting, etc., the risk of a serious loss is incurred. In bullion transactions, beyond all others, petty and unwise economy is surprising. The innovation above mentioned is especially dangerous to the purchaser, as the temptation to practise fraudulent adulteration is thereby greatly increased. By accepting such large masses of precious metal, as imported from abroad, without taking the precautions which formerly were considered necessary, the purchaser runs the risk of paying at the rate of silver for any base metal which may exist in the interior of such bars; and it is easily conceivable that some well-known alloy, closely resembling silver in appearance, might be imbedded, during casting or otherwise, in the interior of

the bars, and not be detected even by cutting them in two. Great frauds might thus be perpetrated, and the victims have no chance of obtaining compensation. It occasionally happens that in solid bars, as well as in "Piña" silver, large pieces of iron are found in the interior; and if this kind of robbery has been to some extent successful, it is not likely that the thieves of the present day, who display so much ingenuity in their criminal profession, will forego the opportunity of engaging in such a highly remunerative business as the adulteration of silver in the manner described. It seems opportune to direct attention to this matter, and it remains for English refiners, who would be the greatest sufferers, to take such measures as may best conduce to the protection of their interests.

SEPARATION OF SILVER FROM METALLIC COPPER BY THE LIQUATION PROCESS.

This process is, probably, of very ancient date, and, as Karsten remarks, where and when it originated is quite unknown. The earliest description which I have found of this process is that in Biringuccio's remarkable treatise on Metallurgy, published at Venice in 1540, under the title of "De la Pirotechnia" (fol. 53, but not Pyrotechny in the modern sense), though it was probably in use long previously; and the next that in Agricola's well-known work, entitled "De Re Metallicâ," first published in 1555. But the most satisfactory old account of it is given by Schlüter in his magnificent folio volume entitled "Gründlicher Unterricht von Hütte-Werken," published in 1738, and of that account I shall largely avail myself in the following pages; for there has been no subsequent material change, at least in German smelting-works, either in the apparatus used or in the mode of conducting the process; and, indeed, no change, so far as is known, for centuries past. The German name for this process is "Das Saigern," a verb used substantively, which means "The Trickling."

In the smelting of argentiferous copper ores, like those, for example, of Mansfeld in Prussia, the silver will be found in the resulting metallic copper; and formerly such copper was generally desilverized by the liquation process at the works where the smelting was conducted. But in recent times the silver has been extracted from the copper regulus, which is always formed in the smelting of sulphuretted copper ores before the separation of copper in the metallic state occurs; and this course has, on account of its superiority in a financial point of view, been substituted for the ancient process of liquation. Whether this process be now practised anywhere in Europe, I am unable to state; but it is still in use in Japan, as will be seen in the sequel.

The principle of the process is founded on the fact, that when a mass, consisting of an intimate mixture by fusion of argentiferous copper and a large excess of lead, is heated to or above the melting-point of lead, but below the melting-point of copper, the lead will *liquate* or flow away in a molten state, and carry with it the greater part of the silver which the copper contained; so that this silver may afterwards be extracted from the lead by the simple process of cupellation. The effect of heat upon the mixture of copper and lead has been described in the Author's volume on the Metallurgy of Lead (p. 91), which, as previously stated, is to be regarded as introductory to this volume on the Metallurgy of Silver.

However carefully the liquation may be conducted, the residual copper always retains a considerable quantity of lead and a proportionate quantity of silver; and it is, therefore, necessary to subject this copper to further treatment of a particular kind in order to extract from it as much of the silver as possible, with due regard to profit and loss.

The process of liquation will be treated under the following heads:—

I. Preparation of the mixture of argentiferous copper and lead, or the Leading.
II. Liquation of the mixture.
III. Treatment of the residual copper from the liquation of the mixture, or the Drying process.
IV. Treatment of the oxidized and accessory products.

I. PREPARATION OF THE MIXTURE OF ARGENTIFEROUS COPPER AND LEAD, OR THE LEADING.

PROPORTIONS OF ARGENTIFEROUS COPPER AND LEAD.

In order that the process of liquation should yield the best result, it is essential, according to the old metallurgists, that the copper, silver, and lead should be present in nearly the following relative proportions by weight; namely, 3 parts of copper to 11 parts of lead, and 1 part of silver to about 500 parts of lead (*i.e.*, 1 loth or about $\frac{1}{2}$ oz. of silver to 15 or 16 lbs. of lead), so that a ton of the mixture of lead and copper contains from about 64 to 68 ozs. of silver. The argentiferous copper and lead are melted together in the manner to be hereafter described, and cast into cylindrical cheese-shaped masses, weighing about 350 lbs. each, which will in future be termed liquation cakes, or simply, the cakes. The proportions stated above were prescribed by Schlüter in 1738 for the composition of an ordinary liquation cake. Thus he writes:—Every liquation cake ought always to contain 75 lbs. of pure copper and 275 lbs. of lead (*i.e.* in the ratio of 3 : 10·98), and 9 ozs. of silver, or at most $9\frac{1}{2}$ ozs. If the proportion of copper be less than above stated, and any error should be committed in the management of the operation, the cakes would be too fusible, and the copper would melt along with the lead; and if the proportion of silver to lead be greater than above stated,

too much silver would be left in the copper after liquation. Another reason for not exceeding the proportion of lead above stated is, that then too much copper would be carried away by the lead, and there would be unnecessary loss of that metal.[1]

According to Kerl, the liquation cakes at smelting-works in the Upper Harz consisted of 100 lbs. of black or unrefined copper, containing from 3 to 5 loths of silver (1 loth = about $\frac{1}{2}$ oz. troy), and from 200 to 250 lbs. of lead; that is, 3 parts of copper to 6 or 7·5 parts of lead (1 lb. Hanoverian = 7217·886 troy grains, and is the same as the old Prussian pound, and 1 loth = 225·55594 troy grains); and it was found from the experience of many years that these proportions gave the best results as to the yield of metal.[2] These proportions, it will be observed, differ considerably from those so strongly insisted on by the old metallurgists, and which they maintained could not be varied, except to a very limited extent, without disadvantage. But, as Kerl remarks, the smelter in compounding his liquation cakes has to consider whether, with respect to the value of the metals, it would be most profitable to save as much copper as possible by sacrificing some lead and silver, or the converse.

When the copper does not contain sufficient silver to produce liquated lead of the degree of richness above mentioned, liquation may be repeated with fresh copper, but with the *same* lead as used in the first operation; or, if poor argentiferous lead be available, it may be added instead of non-argentiferous lead, in such proportions as may be requisite to give to the liquation cakes the prescribed composition. It is hardly necessary to state that, in compounding liquation cakes, account should be taken of the silver existing in the lead, and of the lead which may be present in the copper. When, on the other hand, copper, too rich in silver to be desilverized by a single liquation, has to be treated, various argentiferous products obtained in the processes following liquation may be so mixed and worked up with the rich copper as to produce cakes which may be satisfactorily desilverized in a single liquation. In order that a single liquation may suffice, the proportion of silver, according to Karsten, should not exceed from 19 to 20 loths per centner (*i.e.* from 194 to 204 ozs. per ton); but, according to Schlüter, a cake may contain 20 loths, *i.e.* 25 loths per centner.

Kerl asserts it as a fact, that by one fusion of argentiferous copper with non-argentiferous lead, the extraction of the silver is far more complete than by two fusions with argentiferous lead. In the first case, lead poorer in silver is obtained than in the second case; but the desilverization of the black-copper is more perfect, because the lead retained in the copper after liquation is less rich in silver. Hence, in choosing between these two methods, the question arises

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[1] Karsten, System der Metallurgie, 5. p. 422.

[2] Handbuch der metallurgischen Hüttenkunde, 1865, 4. p. 105. In the first edition, vol. 3. p. 116, published in 1855, the proportions are stated to be 100 parts of copper to 200–257 parts of lead.

whether the greater yield of silver in the first will cover the greater loss of lead in cupellation.

At Oker, previously to 1838, according to Kerl, there were three kinds of mixing or "Frischen"—poor, medium, and rich; but after that time the second was abandoned, because it was found that by twice using the *same* lead, which was at first free from silver, the greater yield of silver covered the greater loss of lead in cupellation. Moreover, this practice was found to be preferable to using the *same* lead a third time, because by the more frequent addition of fresh lead antimony was extracted in larger quantity from the black-copper, and consequently the refined copper was of better quality. A poor liquation cake at Oker consisted of 72 lbs. of copper and 225 lbs. of lead, and a rich one of 72 lbs. of copper and 275 lbs. of lead, whence it appears that in the former the proportion of lead is smaller, and in the latter larger than 11 : 3, being 9·4 : 3 and 11·5 : 3 respectively. The copper operated upon was of two kinds; one produced in copper-smelting and treated in the manner to be presently described, which contained on the average 5 loths of silver per centner, and the other derived from a lead-regulus produced in lead-smelting, which contained from 6 to 6½ loths per centner. The *poor* liquated lead contained 2½ loths and the *rich* 3½ loths of silver per centner, and from 2 to 3 per cent. of copper.[3]

When the process has been carefully conducted, the copper left in the liquated cakes will seldom retain less than 1½ loth of silver per centner (*i.e.* 15 ozs. per ton), and may amount to 3 loths if the prescribed relation in weight between the lead and silver be too far deviated from.

According to Karsten, copper which only contains 8 or 9 loths of silver cannot be directly liquated with profit; whereas, according to Kerl, it was found profitable in the Upper Harz to subject to direct liquation copper containing only from 4½ to 5 loths of silver per centner (5 loths per centner = about 51 ozs. per ton).[4]

In order that the process may be most profitably conducted, exact determinations should be made of the proportions of silver not only in the copper and lead originally used in compounding the cakes, but also in the argentiferous mixtures of lead and copper, which are obtained as by-products in the various operations following the first treatment of the liquation cakes, so that these products may be turned to the best account by using them in fresh liquation cakes or otherwise. According to Karsten, by injudicious management in this respect, the loss of lead may amount to nearly 50 per cent. of the copper operated upon, whereas, by judicious management, it may be considerably reduced.[5]

The copper usually operated upon is the "black-copper" (*Schwarzkupfer* of the Germans), or unrefined copper, which is always very impure, as compared with the same copper refined. By way o

[3] Op. cit., 4. p. 106. [4] Idem, 1865. 4. p. 103.
[5] System der Metallurgie, 5. p. 425.

examples the following analyses of black-copper from different localities are given :—

Composition of Black-Copper.

	I.	II.	III.
Copper	95·45	92·83	67·14
Iron	3·50	1·38	3·31
Lead	—	2·79	20·75
Silver	0·49	0·26	0·41
Zinc	—	—	0·91
Nickel	—	1·05	3·40
Cobalt	—	—	—
Arsenic	—	—	2·00
Antimony	—	—	1·53
Bismuth	—	—	0·30
Sulphur	0·56	1·07	0·25
	100·00	99·38	100·00

No. I. By Berthier.[6] No trace of either nickel or cobalt was found. No. II. By Ebbinghaus, in Rammelsberg's laboratory.[7] The copper in both analyses was produced at the Mansfeld Copper Works before the present methods of desilverizing the copper-regulus were introduced. The silver in No. I. amounts to 160 ozs. 1 dwt. 8 grs. per ton, and in No. II. to 84 ozs. 18 dwts. 16 grs. per ton. No. III. By Lampadius, from the "Muldener Hütte," Freiberg.[8] The silver amounts to 133 ozs. 18 dwts. 16 grs. per ton.

A specimen of black-copper in my collection, from the Hettstädt liquation works, contains 0·4667 per cent. of silver, or 152 ozs. 9 dwts. 3 grs. per ton.

Very impure copper is unsuitable for direct liquation, nor should the lead used in the process be very impure. This is a point to which the old metallurgists direct special attention. It should be borne in mind that in the liquation process the metallurgist has to consider not only the extraction of silver, but the production of copper fit for the market; so that, supposing the argentiferous black-copper be such as would become good merchantable copper by subjecting it to the usual process of refining, it might be entirely spoiled if previously liquated and very impure lead were used in its liquation. The following remarks of Schlüter on the subject are here appropriate:—"Great care must be taken that the bad copper does not spoil the lead which is added to it, and that, on the other hand, the bad quality of the lead does not deprive the copper of its malleability. Hence, all the substances which are concerned in liquation ought to be assayed with care; for litharge and lead which have been derived from ore charged with antimony, arsenic, or cobalt, are capable of spoiling the best copper, because those metals can never be wholly

[6] Annales des Mines, 1st series, 1824. 9. p. 68.

[7] Lehrbuch der chemischen Metallurgie, von C. F. Rammelsberg, 2nd ed. 1865. p. 303.

[8] Op. cit., 1865. 1. p. 735.

separated in the refining of the copper. If a certain quantity of such bad lead were mixed with other matters containing lead which should be in stock for liquation, it might spoil all the stock, and it would be then very difficult to remedy the evil: consequently it is proper that only the purest lead should be kept in store."

THE PREPARATION OF THE MIXTURE OF ARGENTIFEROUS COPPER AND LEAD, OR THE LEADING.

This operation is termed by the Germans "Frischen," which, literally translated, means "refreshing" or "reviving," the latter being applied at British lead-smelting works to the process of reducing litharge. In the case in question, the word means mixing copper and lead together by fusion. I propose, however, to designate it by the word "leading" (previously used in this volume, see p. 250).[1] The leading is[1] generally effected in small blast-furnaces, not unlike the North of England slag-hearth, described in the volume on the Metallurgy of Lead by the Author (pp. 411 et seq.). But they differ from the slag-hearth in the following particulars:—They are somewhat higher; the bed is made of a mixture of charcoal-powder and clay, and slopes downwards from the back or twyer side to the front where there is a tap-hole; outside the furnace, under this tap-hole there is a shallow circular pit or fore-hearth, lined with a mixture of three parts of charcoal-powder and one of clay; and at the bottom of this pit is a tap-hole leading to an open cylindrical ingot-mould or casting-pan, each large enough for one liquation cake. The casting-pan is made either of copper or cast-iron, but usually of copper. The liquation cakes are about 2 ft. in diameter and from 3 to 3½ in. thick, these dimensions having been found from long experience to be the most suitable in every respect.

The form and dimensions of the cakes are not so indifferent a matter as it might seem. The cake-like form is stated to be essential for the separation of as much lead as is generally possible by this process. The dimensions of the cakes are also important; if too massive, it would be necessary towards the last to raise the temperature so high as possibly to melt them; and if, on the contrary, not massive and strong enough to support themselves, they would also be liable to melt down, even if the process of liquation were managed with the greatest care.[2] Further, convenience in handling must be considered, and this is a point on which the older metallurgists insist. The experience of centuries has shown that the

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[1] In Johnson's Dictionary, published in 1805, I find the verb "to lead," of which the meaning is stated to be "to fit with lead in any manner:" it is also in Webster's Dictionary. In the former, the following verse from Ecclesiasticus is cited, which refers to the work of the potter:—"He fashioneth the clay with his arm, he applieth himself to lead it over; and he is diligent to make clean the furnace," xxxviii. 30. The reference is, probably, to the glazing of pottery with lead, and not to covering with lead, which, in this case, is unintelligible.

[1] I shall generally use the present tense in the following description, though the processes described may have been abandoned.

[2] Karsten's Archiv, 1st series, 9. 18.

m, dimensions, and weight, previously stated, best fulfil all the ditions required.[3]

In order to ensure uniformity of composition in the liquation es, only sufficient copper and lead should be melted at a time to m a single cake. The copper should not be in too large pieces, as hat case the period of fusion would be needlessly prolonged, with roportionate increase in the cost of the process. If the copper be tough or too massive to be broken while cold, it is heated to bright ness, and then broken into lumps of the proper size. In old allurgical treatises are engravings of a stamp, with a wedge-ped head, which was used for that purpose. According to Kerl, en black-copper containing lead is so treated, a leady mass not frequently oozes out which is fit for direct cupellation.[4]

[At Oker, in the Lower Harz, the black-copper was used in the nulated state, after having been refined in what is termed a pleissofen," which is a kind of German cupellation furnace. The lowing description of the process is given by Kerl.[5] A charge of centners of black-copper is brought to a red-heat in 3 or 4 hours, ter which the blast is let on and continued for 12 or 15 hours until sion takes place, the slag being constantly drawn off until it is und by the usual mode of testing (previously described by the uthor in the volume containing the subject of Copper-smelting) that e copper is sufficiently refined, when it is tapped off and granulated water. The yield of granulated copper, which contains 5 loths of lver per centner, is 52 centners.[6]

According to the foregoing description, the blast is continued for 2 or 15 hours *until* fusion occurs, and the slag is constantly drawn f during the process; but no slag, properly so called, would be roduced previously to fusion. Winkler saw this process in operation t Oker in 1830, and has published a plain and intelligible account f it, to which Kerl refers, and from which the following extract is ken:—Forty centners of black-copper are "blown" (*i.e.* exposed to e action of a blast) at a time, and the blast is first let on when the pper has become red-hot throughout. After about 6 hours, the pper is completely melted, and continues, thus molten, to be exposed the action of the blast for several hours, whereby it nearly attains e completely refined state, from 8 to 10 centners of slag having en formed and drawn off during that period.[7] When this process

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[3] According to Karsten, the cakes may y in diameter from 24 to 26 inches ussian), in thickness from 3 to 3½ hes, and in weight from 3½ to 3½ ntner (Prussian). Idem. 1 Prussian t = 1·02972 English = 0·31385 metre; 1 centner = 103·111 lbs. avoirdupois. Handbuch, 4. p. 104.

[4] Idem. 4. p. 114. [6] Idem.

[5] Erdmann's Journal für technische ökonomische Chemie, 1831. 12. p. The granulation process had been in use at the Frau Marien Liquation Works near Goslar (at Oker, in the vicinity of the town of Goslar) some years before Winkler visited them, and was adopted with the special object of rendering the copper more favourable in shape for mixing with lead in the Leading process. But the chief advantage was derived from the re-melting of the metal, whereby it was made purer by the separation of a quantity of iron, zinc, and sulphur. Re-melting was effected in a

is finished, the copper is tapped by making a hole in the dam, and flows into the granulating tub. Winkler expatiates on the danger from explosions in this operation, and of the necessity of taking various precautions, which, he says, are unnecessary (?) in granulating cast-iron. In order to have good grains the molten copper must run in a thin stream, while the water is kept in violent agitation. If this agitation be feeble, only compact grains and lumps are obtained, which are leaded with much greater difficulty than broken up black-copper; and if the copper-stream be too strong though the water be violently agitated, small yet much too compact grains are produced. The grains ought not only to be small, but thin and as porous as possible. The agitation of the water is effected by running a stream of water into the tub, with the gutter so adjusted that the two streams of water and copper may meet, after they have fallen a short distance. It is hardly necessary to state that provision is made for the outflow of water from the tub as fast as it runs in. The whole granulation process lasts several hours and it is attended with loud detonations and a noise like that of the most powerful small-arms. The grains retain water (according to Kerl about 10 per cent.[8]) for a long time in their pores. The advantage of using granulated copper has not proved so great as was expected.]

The furnace is first duly heated throughout, as is also the casting-pan, which should be previously coated internally with a wash of clay, and then dried; after which from 4 to 5 cubic feet of charcoal are thrown in, the blast is turned on, and at the same time about ½ centner of slag from a previous leading (or, according to Schlüter, slag from copper-smelting) is added. As soon as the slag appears in the hearth, a quantity of copper sufficient for the first liquation cake is introduced; and when, after the lapse of four or five minutes, it has become red-hot, the proper quantity of lead is added. The alloy soon reaches the fore-hearth, and accumulates under the liquid slag contained therein. Directly afterwards 1¾ cubic foot of charcoal, ½ centner of slag, and a quantity of copper sufficient for the next liquation cake are thrown into the furnace in the order stated. By this time the fore-hearth will be filled with metal, which should be very hot and run very liquid, and which may then be tapped off into the casting-pan, an iron hook or ring having been previously set upright in the pan, by means of which the liquation cake, after solidification, may be attached by a

"Spleissofen;" the hearth or bed of the furnace is about 7′ in diameter; and nearly at right angles to the direction of the blast, and opposite the fire-place, there is a channel in brick or stone work which leads to the granulation tub sunk in the ground, the channel being solidly lined with a mixture of clay and charcoal dust. The hearth, which is made of the same kind of mixture lightly beaten down, is nearly flat, and slopes from 1″ to 1½″ towards the tap-hole, which, during the process, is kept dammed up also with this mixture. In the wall nearly opposite the blast is an opening for drawing out the slag. The granulation tub, which is made of wood, is oval, 8′ long, 6′ wide, and 6′ deep. Over the rim of the tub is an inclined gutter, which reaches nearly to the centre, and is intended for supplying water.

[8] Die Rammelsberger Hüttenprozesse, 1854. p. 99.

chain to a crane or other apparatus, and so hoisted and deposited at a convenient distance. The hook or ring appears to have been pulled out before liquation of the cakes commenced, as may be inferred from the holes shown in the cakes in Ercker's engraving (p. 313). Immediately before tapping, the proper quantity of copper for the next liquation should be put into the furnace, so that the work may go on uninterruptedly. The metal in the pan is solidified as quickly as possible by sprinkling water upon it, in order, as far as possible, to prevent any separation of the copper and lead from each other during cooling. The solidified cake is taken away in the manner above mentioned, and the casting-pan washed over with a mixture of clay and water, to be ready for the next tapping. When the work goes on well, each liquation cake is produced in 7 or 8 minutes. At Neustadt-on-Dosse, Brandenburg, Prussia, about 60 cubic feet of charcoal were consumed in preparing 100 centners of the cakes. Other statements concerning the consumption of fuel will be given in a tabulated form in the sequel, from which it will be seen that the consumption of charcoal at Neustadt differs materially from that at other liquation works. The same series of manipulations is repeated until the last liquation piece is cast; after which the breast of the furnace is opened to the height of about 1½ ft. above the fore-hearth, in order that any slag and bits of metal remaining in the furnace may be drawn out with an iron crook.

The operation of leading with litharge, instead of metallic lead, is effected in the same kind of furnace as that above described; but a longer time is required in order that the litharge may be completely reduced. Karsten states that at Neustadt the fuel used in this mode of leading consisted of a mixture of charcoal and coke, and that only one liquation cake was produced in about 40 minutes, which accounts for the comparatively large quantity of fuel consumed.

Physical Characters and Chemical Composition of the Slag (*Frischschlacke*).

Specimens in my collection from Hettstädt and the Rammelsberg[*] are both alike, glassy, conchoidal in fracture, and brown-black veined with brownish-red.

This slag is a silicate of very variable composition, containing, according to Karsten, from 40 to 60 per cent. of lead, and from 3 to 5 per cent. of copper; it is afterwards treated along with other accessory products, with a view to extract from it as much lead and copper as possible. Karsten analysed a sample of this kind of slag, prepared from a mixture of specimens taken at intervals during a working shift of 12 hours, and found its composition to be as follows:[1]—

[*] Rammelsberg is a mountain at the foot of which is the town of Goslar.

[1] Archiv für Bergbau und Hüttenwesen, 1st series, 1825. 9. p. 24.

COMPOSITION OF THE SLAG PRODUCED IN THE LEADING PROCESS (*Frischschlacke*).

	Per cent.
Oxide of lead (PbO)	63·2
Cuprous oxide	5·1
Silica	20·1
Ferrous oxide	6·8
Alumina	4·7
	99·9

Potash was sought for, but not detected. The ratio between the oxygen of the silica and that of the bases is, approximately, 2 : 1.

Karsten states, that even when no slag is added in the leading process in the blast-furnace, the formation of each cake is always attended with the production of about 5 or 6 per cent. of slag, the silica being derived from the ashes of the fuel and the furnace lining, and the alumina from the latter alone.

PREPARATION OF THE MIXTURE IN REVERBERATORY FURNACES.

The mixture may be made in a reverberatory furnace; but the use of such furnaces for this purpose is exceedingly restricted, according to Karsten, to whom we are indebted for the following observations on the subject. The copper is first melted, and then the requisite quantity of lead is thrown in. Although the lead is almost instantaneously melted, yet it is necessary further strongly to heat the metallic mixture in order to stir it while in a very liquid state. The metal is tapped into moulds of the usual form. According to the size of the furnace, 6, 10, or more cakes may be made in a single melting. But the profitable working up of the oxidized leady products, which are obtained in large quantity in liquation works, is of the highest importance; and for that purpose, according to Karsten, blast-furnaces are essential. Besides, in reverberatory furnaces, waste products or furnace residua are formed in larger quantity than in blast-furnaces: so that, apart from local conditions, especially the kind of fuel available, the latter are preferable to the former.

II. LIQUATION OF THE MIXTURE.

DESCRIPTION OF THE LIQUATION FURNACE OR HEARTH.

A simple form of this furnace or hearth is shown in the quaint, yet very intelligible woodcut, fig. 49, copied from a larger woodcut in the original metallurgical treatise in German of Lazarus Ercker,[2]

[2] Aula Subterranea Domina Dominantium Subdita Subditorum. Das ist: Untererdische Hofhaltung ohne welche weder die Herren regieren, noch die Underthanen gehorchen Können. Franckfurt, 1736, a late edition, p. 147.

f which a translation into English was made and published by Sir ohn Pettus in London 1686.[a]

The following description is founded mainly on that of Schlüter: -There are two low, short, massive, parallel walls of brick or stone ork, which incline towards each other from below upwards; their

Fig. 49. Liquation furnace.

A. "Die Seiger-Oefen," or liquation furnaces. B. "Die Seigerscharten," of cast copper (the German word is so spelt in the original work; the word "Scharte" in German means literally a notch, so that probably the word "Seigerscharte" came to be technically applied to plates notched, as it were, on the sides in the manner shown in fig. 50). C. "Die Seigerstück," liquation blocks or cakes. D. "Die Seigerwend," end and side plates. E. "Der Seigerer," liquator or man who manages the liquation. F. "Die Kupffern oder eisern Pfännlein," the little pans of copper or iron. G. "Die Künstock," the blocks or cakes after liquation. H. "Der Zua," crane, with which the liquation cakes are lifted into the furnace.

er surfaces are flat and slope downwards from back to front, as as inwards, but do not touch each other, a space of about several es being left between them at the top from end to end, and of t a foot or more at the bottom; at the back the walls abut on a massive chimney, communicating below with the passage bounded

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[a] Fleta Minor. The Laws of Art and re, in Knowing, Judging, Assaying, g, Refining, and Inlarging the s of Confin'd Metals. By Sir *John* s of *Suffolk*, Kt. Of the *Society* for the Mines Royal. Illustrated with 44 *Sculptures*. London, MDCLXXXVI. Folio. The "sculptures" are copper-plate engravings, and fairly represent the spirit of the original woodcuts.

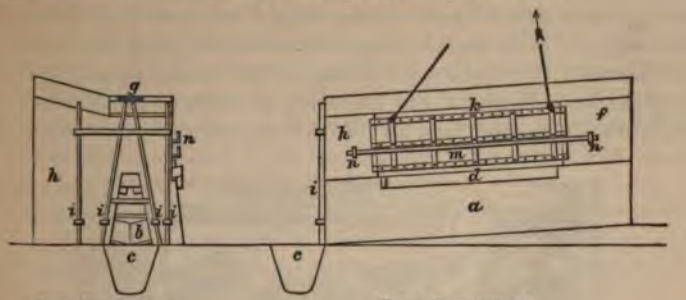
by the two walls above described. The bottom of this passage is solidly lined with clay, in order to prevent the liquated lead from reaching the foundation of mason-work underneath; and it is made to slope downwards from back to front about 6 to 8 inches, and from each side towards the median line, so that any molten metal which drops from above may flow forwards into a circular pit in front of the furnace: this pit is also solidly lined with a mixture of clay and charcoal-dust, and it is recommended that it should be large enough to receive the whole of the metal liquated in one operation, in order that all the ingots of this metal may contain as nearly as possible the same proportion of silver. The furnace is built on a solid foundation of brick or stone work. On the top of each wall is fixed a plate of cast-copper or of cast-iron, about $3\frac{1}{2}$ inches thick; these bed-plates are either of the same width from end, in which case they are kept about $1\frac{1}{2}$ inch apart by the insertion of a piece of iron between them at each end, or they have the form shown in fig. 50: in the latter case, it will be seen that the plates touch both at the ends and in the middle. When, in the course of working, the plates have become so much burnt away on their inner edges as to be no longer fit for use, they are turned with their outer edges inwards. The upper part of the furnace consists of three movable plates, two long and one short, of strong sheet-iron; a sort of rectangular trough is thus formed, the end at the back being the chimney on which the furnace abuts. The plates are strengthened along their edges by iron bars riveted to them, and sometimes additionally strengthened, in order to prevent warping, by iron bars placed crosswise; in some of the old descriptions they are stated to have been studded over with little bent hook-like bits of iron, in order to hold fast a lining of clay on their inner surfaces. The plates are kept together by iron bars, placed horizontally on the outside, and fixed at their ends by means of eyes and cotters or otherwise. The liquated lead is laded into shallow circular pans of either copper or iron, and thus cast into forms suitable for the old German method of cupellation. Near the front end of the furnace there is a cistern or pit containing water for cooling tools, etc.; and a crane, for hoisting the liquation cakes.

Fig. 50. Bed-plates of the liquation furnace. Copied from Schlüter's engraving.

In the annexed woodcuts, copied from the engravings numbered 950, 951, 952, 953, 954, 955, in the Atlas belonging to Karsten's "System der Metallurgie," is represented the furnace which was used for liquation at Neustadt-on-Dosse, where he seems chiefly to have studied the process.

There seems to have been not a little diversity in minor details in the construction of this furnace; for I have referred to every old and modern work, containing an account of the process of liquation and engravings of the furnace, which I have been able to consult, and have not found any two representations of it alike in all respects, exce

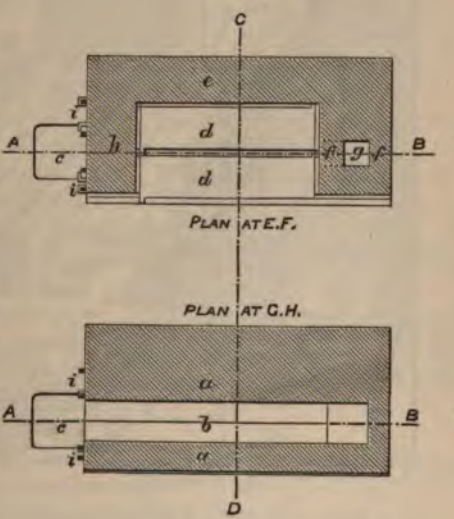
when one author has copied from another. Excellent engravings of such a kind of liquation furnace as described above will be found in Schlüter's volume, to which I have previously referred.



END ELEVATION.
Fig. 51.

SIDE ELEVATION.
Fig. 52.

a a. Walls, between which is the passage.
b. Cast-iron plates forming the floor of the passage.
c. Receiving-pit.
d d. Cast-iron bed-plates, 1½ in. apart at their inner edges, and inclining 4 in. from back to front.
e. Side wall of brickwork.
f f. Back wall of chimney.
g. Flue communicating below with the back end of the passage.
h. Front-end wall of brickwork.
i i. Iron bars for supporting h.
k. Side or door of sheet-iron, raised or lowered by a lever.
m. Iron bar for supporting k.
n n. Hooks which hold m in its position.



PLAN AT E.F.
Fig. 53.

PLAN AT G.H.
Fig. 54.

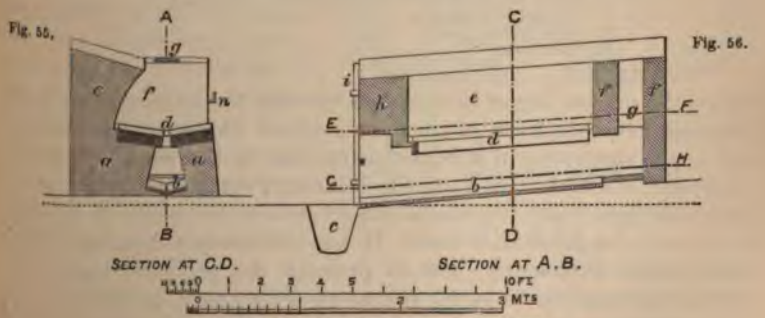


Fig. 55.

Fig. 56.

SECTION AT C.D.

SECTION AT A.B.

Figs. 51-56. Liquation furnace at Neustadt.

Attention should be directed to the chimney at the back of the furnace, and to its connection with the space between the two walls

The object of this chimney, Schlüter distinctly states, is to increase the draught when necessary; and if so, there might possibly have been a *down* draught from the furnace into the passage between the walls, in which case the mouth of the passage could not have been left entirely open. Indeed, it is stated that a charcoal fire was kept up in the space between the walls as well as in the receiving-pit. Thus in a description by Manès of the liquation process, as practised at Hettstädt, which was published in 1824, it is expressly mentioned that

Fig. 57. Liquation furnace.

A. Fornax in qua opus secernendi perficitur (furnace in operation).
B. Fornax in qua non perficitur (furnace not in operation).
C. Catinus (receiving-pit).
D. Catilli (casting pans).
E. Panes (cakes).

before the process began the passage between the walls was filled with charcoal, and that fresh charcoal was added during the operation;[4] and in the engraving of a liquation furnace in the work of Héron de Villefosse, entitled "La Richesse Minérale," and published in 1819 (plate 58, figs. 7 and 10), the passage between the walls at the front is shown to be filled with fuel. It was obviously necessary to keep the passage sufficiently hot to prevent the liquated metal from solidifying therein. But in Héron de Villefosse's engraving there is also shown an opening through the front of the chimney, so much

[4] Notice sur les Mines de Schiste Cuivreux et sur les Usines du Pays de Mansfeld. Par M. Manès. Annales des Mines, 1824. 9. p. 40.

above that end of the furnace, that I cannot understand its function, unless, when opened, it acted like a damper, and checked the upward current in the chimney from below. But the draught above referred to may mean that *through* the passage to the chimney; and if so, the notion with respect to a *down* draught is untenable. A draught through the passage, however, would divert some of the air which enters it, from its course to the furnace above, and so lower the temperature therein. In the engravings in the treatises of Agricola and Ercker, there appears to be no chimney, but only a solid mass of brick or stone work.

The figure of a liquation furnace on p. 316 is copied from a woodcut in Agricola's treatise (*De Re Metallicâ*, lib. xi.). The lower part of the original engraving has been omitted in the copy; and in the latter there are one or two inaccuracies, but not of any importance.

The liquation furnace of which Biringuccio published an account in 1540, and gave an illustrative woodcut, is similar to that figured by Ercker, except that the ends and one of the sides are formed of a lattice of iron bars, fixed to an outer frame of iron, while the other side is formed of permanent brick or stone work; and it is directed to take care to make the spaces between the bars small enough to prevent the pieces of charcoal from falling through them.

Reverberatory liquation furnaces.—Such a furnace was in use at Hettstädt, and is represented in fig. 58, copied from the engravings given by Héron de Villefosse.[5] It is shown in vertical longitudinal section and in plan; the latter is taken a little above the grate, and shows a central doorway through which the cakes were introduced and the liquated copper drawn out: the doorway for charging the fuel is not shown in the plan. Nothing is stated concerning the working of the furnace; but it strikes me that it would be no easy matter to adjust such heavy masses as liquation cakes in this kind of furnace, as a man would have to creep into the interior for that purpose, and work in a very cramped position.

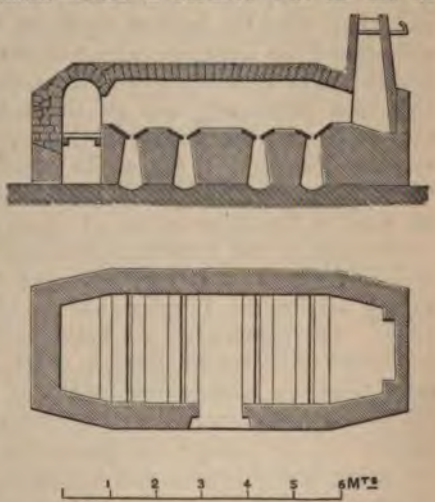


Fig. 58. Réverberatory liquation furnace.

Schlüter in 1735 was the first to apply the reverberatory principle of heating to the liquation process at smelting-works in the Lower Harz; and in his work is a set of excellent engravings of a furnace which he constructed on that principle (plate 49). His

[5] De la Richesse Minérale. Atlas, plate 58, figs. 11 and 12.

object was to substitute wood for charcoal, in localities where the latter was dear. It differs greatly from the furnace at Hettstädt: let the reader imagine a Bleiberg lead-smelting furnace (of which engravings and a description are given in the Author's volume on the Metallurgy of Lead), of which the bed is replaced by a primitive liquation hearth, such as I have described, the side on the right open from end to end, and this opening fitted with a sheet-iron door, suspended by a chain passing over a pulley and connected with a winch, so that the door could be raised or lowered at will, and he will have a tolerably correct notion of Schluter's furnace. The fireplace on the left extends the whole length of the furnace, and the flame from it passes towards the right, partly downwards into the passage between the walls, and thence upwards through a vertical flue at the back, and partly from under the suspended sheet-iron door, which, as will be seen further on, was not kept fully lowered during the process. The cakes are introduced through the side opening on the right by means of strong long-handled tongs suspended by a chain, just as in some re-heating furnaces now in use at ironworks. Wood was the fuel employed. Twelve liquation cakes are treated at a time in this furnace; and between them, as well as on each side of them, pieces of wood are packed. The suspended door is lowered only so far as to close the upper part of the side opening. The fire is now lighted; and when, after the lapse of about an hour or less, the wood between and around the liquation cakes has become ignited, the door is further lowered until it rests on two bricks, placed one over the other, which had been previously laid on the bottom of the side opening, so that an open space is left in that opening from end to end, which remains open during the whole period of liquation. The edges of the sides and top of the door are not luted with clay, in order to let some of the flame escape at those edges. There is a hole in the upper part of the brickwork forming the front end of the furnace, which is left open at the beginning of the process, with a view to supply air to the interior, but is afterwards stopped up with a brick. The pieces of wood between the cakes being ignited, wood is thrown into the fireplace in order to increase the heat. At the same time the passage and bottom of the furnace [*i.e.*, I presume, of the passage] are heated pretty strongly, so that flame may issue from the front of the passage, the flue at the back being stopped, to prevent its taking that direction, and to compel it to pass between the cakes. When the cakes towards the front begin to liquate, the upper hole mentioned above, is closed with a brick, in order that the flame may be made to return over these cakes.

Genssane designed a circular furnace, with a movable cover, as in the German cupellation furnace, in which coal should be used for fuel; but it does not appear that such a furnace was ever constructed.[*]

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[*] Traité de la Fonte des Mines par le Feu du Charbon de Terre, 1770 1. pp. 149 et seq. Minute directions are given for the building of this furnace, together with three illustrative copper-plate engravings, Nos. 18, 19, and 20.

He was of opinion that Schlüter was right in recommending the application of the reverberatory principle to the liquation furnace, because "one is master of the heat necessary to be given, which is not the case in the usual furnaces, where the metal is plunged into the charcoal."[7] According to Karsten, however, the reverberatory principle has often been tried for liquation, but never with satisfactory results, because far too much free atmospheric oxygen comes in contact with the cakes, and it is not possible, with every precaution, to heat the cakes with sufficient uniformity.[8]

MODE OF CONDUCTING THE PROCESS OF LIQUATION.

The following description of the mode of conducting liquation is extracted nearly *verbatim* from Schlüter's treatise:—The upper surfaces of the sloping bed-plates are coated with a mixture of loam or ashes and water, and afterwards sprinkled over with charcoal-dust (charcoal-slack would be a suitable expression), in order to prevent adhesion from taking place between those plates and the liquated copper. The cakes are set upright and crosswise, 6 or 8 inches apart, and the distance between them is, according to Schlüter, determined by the proportion of copper: those which contain most copper stand heat best, and may therefore be set further apart. Pieces of wood are inserted between the cakes in order to prevent their falling upon one another; the side and end plates of sheet-iron, either coated or uncoated with loam, are fixed in their proper position; and pieces of wood are put between the sides of the furnace and the convex sides of the cakes: after which, all the empty space remaining is filled by hand with charcoal, in order that it may tend to keep the cakes erect. The charging is completed by covering the cakes well over with charcoal. Before lighting the furnace the receiving-pit should have been well heated by burning charcoal within it; and should be kept so during the entire process by the addition of fresh charcoal from time to time.

The furnace is lighted by placing live charcoal at the top, and at the same time live charcoal is put into the passage between the walls, in order to make it hot enough to prevent the liquated metal from solidifying in its course to the receiving-pit. When the fire begins to burn well, the flue at the back is closed, because ignition always takes place sooner at the back than at the front of the furnace, and it is better that the fire should begin at the front and spread towards the back. As soon as the liquated metal begins to run towards the front, the flue is re-opened. Great care must be taken that none of the cakes be without charcoal before they begin to sink down, and the charcoal therefore must be renewed as fast as it burns away. Should the fire become too strong, and the copper flow along with the lead, it would be necessary to withdraw all the fire from the passage (*unter dem Herd*), and even to throw in cold small charcoal (*Gestübbe*)

[7] Traité de la Fonte des Mines, etc., 1. p. 150.
[8] Archiv für Bergbau und Hüttenwesen, 1st ser. 1825. 9. p. 25.

to cool it. When, however, but little of the copper flows along with the lead, it is not requisite to withdraw the fire, because this copper may be recovered from the "Saigerdörner" and "Krätzkupfer" (see p. 324 in the sequel); and it is always better to liquate at the highest temperature below that which would melt the copper or cause too much of it to be carried off by the lead, as in that case the silver is more effectually removed by the lead from the copper.

In Hellot's translation of Schlüter's treatise, it is recommended that when the liquation cakes begin to get too hot, one or two pieces of fir-wood should be put into the passage under the cakes, because "the flame of this resinous wood prevents the copper from melting and flowing with the lead and silver."[9] This at first appears to be a puzzling statement, but is not therefore to be summarily rejected as inaccurate. The air, which maintains combustion in the furnace, is obviously supplied, for the most part, through the space between the bed-plates on the walls. Now, by throwing fir-wood into the passage, much steam and smoke would be rapidly evolved from the burning wood, which would lessen the supply of air to the furnace, and so lower its temperature. Orschall, in his article on Liquation published towards the end of the 17th century, mentions this practice, but condemns it as useless. (Œuvres Métallurgiques. Trans. from the German. Paris, 1760, p. 162.)

All the cakes in a liquation furnace ought to shrink down equally and simultaneously; and unless they do so, they would not be well liquated, and the residual copper would retain too much of the silver. If any one of the cakes should not shrink, it would be necessary to surround it again with charcoal, when, in a short time afterwards, it will shrink like the other cakes. But if the furnace be very equally heated throughout, as it should be, all the cakes will shrink simultaneously, and liquation proceed properly. When it is seen that the greater part of the lead has drained off, the fire may be somewhat increased in the passage, to make the cakes yield as much lead, and therefore also as much silver, as possible. Towards the end of the process the lead only runs off drop by drop. According to Karsten, the liquation of eight cakes is completed in 4 or 5 hours.

Before removing the residual masses of copper from the furnace, after liquation has ceased, it is the practice, according to Karsten, to pour water upon them while they are still red-hot, in order to hasten their cooling and save time in getting the furnace ready to receive the next charge; and it is observed that this application of water causes a further squeezing out of lead, as though liquation were beginning again, but it only occurs at a certain temperature when the residual copper is neither too hot nor too cold. The lead which is extruded by thus cooling with water contains 2·9 per cent. of copper, and is somewhat more coppery than that ordinarily liquated, or, what Karsten designates, "clean liquated lead" (*reine Saigerwerke*).[1]

The liquated lead is laded from the receiving-pit into the ingot-

[9] De la Fonte des Mines, 2. p. 535. [1] Archiv, 1st series, 9. pp. 31 and 33.

moulds previously described, to the amount of 50 lbs. in each mould if it be rich enough in silver for direct cupellation; but if not, the ingots should be smaller in order that they may be more easily weighed and apportioned for use in a second liquation. At each lading a small portion of the metal should be put aside; and when the process of liquation is finished, all the portions should be melted together, and a sample taken from the molten mass to be assayed for silver.

During the course of liquation, the bottom of the passage between the walls of the furnace should be frequently cleared in order that the lead may not be stopped in its course, and thereby "burn" or be oxidized. When liquation has ceased, the charcoal that remains in the furnace is left to burn away, after which the sheet-iron sides and end are taken down. The coppery residues of the cakes are removed by means of strong long-handled tongs, but not until their temperature has been lowered to dull redness, because, at a higher temperature, they would easily break into pieces. The residues are put aside for after-treatment.

Any small metalliferous pieces which may be left on the bed-plates, or in the passage underneath, are put into the receiving-pit, which is still very hot, and stirred several times; so that any intermixed argentiferous lead may melt and subside, leaving more coppery metal at the top, which is taken off, and which is designated "liquation thorns" (*Sayger-Dorner* or *Sayger-Kratz*, Schlüter).

The proper regulation of the temperature is essential to the success of the process of liquation, as this is the only means by which the cakes can be thoroughly liquated, without being melted. Too high a temperature towards the end of the process causes an unnecessary waste of copper; because the molten lead would in that case carry off notably more copper, none of which is afterwards recovered, and at the same time there would be no increase in the proportion of silver removed for a given quantity of lead. Moreover, another evil results from too high a temperature towards the end of the process; namely, the production of a much larger quantity of a mixture of oxide of lead and cuprous oxide than occurs at a lower temperature.

It is obviously desirable that neither copper nor lead should be oxidized in this process; and, therefore, access of free atmospheric oxygen to the cakes should as far as practicable be prevented. But, with every precaution, it is not possible wholly to prevent such oxidation, especially towards the end of the process, when the temperature is highest and the cakes are more exposed to direct contact with the air, owing to the burning away of the charcoal. Manès describes the oxidized product as having a stalactitic form.[3] Further observations on this product are given in the sequel, p. 324.

The proportion of silver in the liquated metal varies very little from the beginning to the end of the operation; and the proportion

[3] Annales des Mines, 1824. 9. p. 32.

of copper only fluctuates between 2 and 2·8 per cent., provided the temperature has not been high enough to cause the cakes prematurely to shrink down together.

Karsten collected with great care in a ladle some of the lead as it liquated at seven different periods during the course of a single liquation, such as is usually completed in from 4 to 6 hours. One portion was taken at the beginning, another towards the end of the process, and the remainder at intervals of about 30 minutes. The percentage composition of these seven portions of lead was found to be as follows:[2]—

	I.	II.	III.	IV.	V.	VI.	VII.		Mean.
Lead	97·8	97·9	97·3	97·6	97·1	97·5	97·3	.....	97·5
Copper ...	2·2	2·1	2·7	2·3	2·8	2·5	2·7	.....	2·5

Hence it appears that throughout the process the proportion of copper in the liquated lead is nearly the same, the maximum difference amounting to not more than 0·7 per cent.

The proportion of silver in the liquated lead also remains nearly the same throughout the process. Thus Karsten determined by assay the contents of silver in each of the seven portions above mentioned, and obtained the following results, the figures in the second line indicating the number of loths of silver in 200 lbs. weight of the liquated lead:—

	I.	II.	III.	IV.	V.	VI.	VII.
Loths in 200 lbs. ..	10·5	10·5	10·75	10·75	10·75	10·8	10·8

Computing from the weights used when Karsten wrote, 10·5 loths in 200 lbs. of lead = 0·164 per cent. = 53 ozs. 11 dwts. 11 grs. of silver to the ton.

The residual copper contains, on the average, about one-third of its weight of lead; and even after having been strongly liquated, in which case a large quantity of the mixture of oxide of lead and cuprous oxide is always formed, it retains as much as one-fourth of its weight of lead. The silver, which is left in the residual copper, is in exact proportion to the quantity of lead in that copper, so that it is very easy to compute how much silver is extracted by the liquated lead, and how much is left in the residual copper. Thus, let the weight of silver in a liquation cake, composed of copper and lead in the proportion by weight of 3 : 11, be equal to 1; and let the copper and lead in the residual copper be in the proportion by weight of 2 : 1; then out of 11 parts of silver $1\frac{1}{2}$ part will be left in the residual copper, or about 0·87 of the original silver will pass into the liquated lead, and 0·13 be left in the residual copper. But these proportions of silver, it is hardly necessary to remark, will vary according to the degree in which the liquation of the lead has been effected.

The proportions of residual copper, liquated lead, and oxidized product will vary with the manner in which the process has been

[2] Archiv, 1st series, 9. pp. 28, 29.

conducted; and the conditions which particularly determine those proportions are as follow:—The greater or less rapidity with which the temperature is increased, and the time during which the high temperature towards the end of the process is maintained and the formation of oxidized product thereby promoted. Thus, at one time, from eight liquation cakes may be obtained 18 centners of liquated lead, 8 centners of residual copper, and 1 centner of oxidized product; and at another time, 16 centners of liquated lead, 7 centners of residual copper, and 4½ centners of oxidized product.

At Neustadt, in liquating 100 centners of cakes, 95 cubic feet of charcoal and 36 cubic feet of wood were consumed.[3] Other statements on this subject will be given in a tabular form in the sequel.

PHYSICAL CHARACTERS AND CHEMICAL COMPOSITION OF THE PRODUCTS OF THE PROCESS OF LIQUATION.

Liquated Lead (*Saigerwerk*).—It is lead-like in appearance, but always contains from 2 to 2·8 per cent. of copper, provided the liquation cakes have consisted of the usual proportions of lead and copper, namely, 78·57 per cent. of lead and 21·43 per cent. of copper, and the temperature has not been so high as to have caused the liquation cakes to have prematurely shrunk down together.[4]

Residual copper (*Kiehnstock*).—A specimen in my collection from Hettstädt has the following characters:—When it is freshly fractured, it is seen to be very unhomogeneous, and to consist of a mixture of lead-coloured and copper-coloured metals, not in small grains, but in pieces of comparatively large size. There is an irregularly-shaped cavity in it, from the internal surfaces of which project short pointed pieces, formed apparently by the partially melting away of the metal: pieces which have been compared to teeth, as will be seen further on when the treatment of this residual copper is considered. The appearance of such teeth is a guide as to temperature, and indicates incipient fusion. The specimen in question is termed "rich" (*Reich-Kiehnstock*), and is stated to contain 3½ loths of silver per centner, *i.e.* 35 ozs. 14 dwts. 8 grs. per ton.

A specimen in my collection, also from Hettstädt, which is termed "poor" (*Arm-Kiehnstock*), and is stated to contain 2½ loths of silver per centner (*i.e.* 25 ozs. 10 dwts. 3 grs. per ton), is similar in characters to the last specimen.

A specimen in my collection of the "rich" metal (*Reich-Kiehnstock*), from the Rammelsberg, the proportion of silver in which is not given, is very irregular in form, ragged, porous, black, and as though glazed on the surface; and a specimen of the "poor" metal (*Arm-Kiehnstock*), also from the same locality, is similar in character to the last, with vitreous brown-red slag (*Darrost*) in some of its cavities.

According to Karsten, the residual copper from liquation cakes, composed of the usual proportions of lead and copper—namely, 78·57

[3] Karsten, System der Metallurgie, 5. p. 442.
[4] Idem, 5. pp. 441 and 442.

per cent. of lead and 21·43 per cent. of copper—consists, in general as before stated, of about 70 per cent. of copper and 30 per cent. of lead.[5] The residual copper from very different liquations (*selected verschiedenen Saigerungen*) was analysed by Karsten, and the percentage composition was found to be as follows:—

	I.	II.	III.	IV.	V.
Copper.....	67·1	53·6	70·2	73·1	75·4
Lead.....	32·9	46·4	29·8	26·9	24·6

Nos. III., IV., and V. were from Neustadt, but the names of the works from which the others were obtained are not given.

Liquation in the cases of Nos. I. and II. had evidently been incomplete.

The composition of No. V., which contains the least lead, approximates to that indicated by the formula $Cu^{12}Pb$ [idem]; namely, 78·56 per cent. of copper and 21·44 per cent. of lead. Karsten is disposed to regard the residual copper (*Kiehnstock*) as a definite alloy of copper and lead in those proportions; and he suggests the hypothesis, that in the process of liquation two definite alloys are formed, one of the formula above mentioned, and the other of the formula $CuPb^{12}$ [idem]. Hence, admitting this hypothesis, he infers that the best proportions of copper and lead in a liquation cake are those indicated by the formula

$$Cu^{12}Pb + CuPb^{12} = Cu^{13}Pb^{13}, \text{ or } 13\ CuPb\ [\text{idem}].$$

Calculating from this formula, the ratio between the copper and lead should be as 3 : 9·82; or nearly the same as the ancient metallurgists had adopted.[6] The hypothesis of Karsten will be further considered in the sequel.

Accessory products (*Saigerdörner* and *Saigerkrätzen*).—A specimen in my collection from Hettstädt, labelled "Saigerdörner," may be compared, in outward form, to a cluster of small stalactites, as if produced by the dropping of imperfectly molten matter, like the clinkers which are occasionally found hanging from the bottom of furnace bars; the fractured surface shows more or less porosity of structure; the mass consists of lead-coloured metal with adherent litharge-like stuff, or "Saigerkrätz." Such masses were designated by the old metallurgists "Saigerdörner," or liquation thorns, because they "bristled with points, and in that respect resembled thorns." (Orschall, antea cit. p. 146.)

Another specimen in my collection from the Rammelsberg is slag-like in appearance, very uneven, very brittle, is not stalactitic in form, and has pieces of charcoal imbedded in it. Another specimen from the same locality is light copper-red, and contains evidently much unoxidized metal.

The metal obtained by fusing a sample of "Saigerdörner" with charcoal was found by E. von Szamit to have the following composition per cent.:[7]—

[5] Archiv, 1st series, 9. p. 16. [6] Idem, 9. pp. 30, 31.
[7] Oesterreichische Zeitschrift für Berg. u. Hüttenwesen, 1856. p. 62.

Lead	79·68
Copper	11·93
Antimony	7·30
Silver	0·213045
Gold	0·000465
	99·123510

The ratio between the lead and silver is 500 : 1·33, and not 500 : 1, so that supposing the latter ratio to have existed in the liquation cakes it did not remain constant in the "Saigerdörner." The amount of silver per ton in this product is 69 ozs. 11 dwts. 21 grs.

III. TREATMENT OF THE RESIDUAL COPPER FROM THE LIQUATION OF THE MIXTURE, OR THE DRYING PROCESS.

The residual copper, which, as before stated, retains about 30 per cent. of lead and silver in proportion, is subjected to further treatment, of the nature of liquation, in order to extract from it as much of that lead and silver as possible, with due regard to expense. This treatment consists in exposing the residual copper to a prolonged high temperature in a special furnace, whereby lead is separated almost wholly in the state of molten oxide in association with a notable quantity of cuprous oxide. According to Karsten, it would be possible to conduct this process in the ordinary liquation furnace; but in that case the consumption of fuel would be much larger than in the special furnace now to be described. The German name for this furnace is "Darrofen," which, literally translated into English, is "Drying Oven;" it is derived from the verb "darren," which means to dry in a kiln, as in the drying of malt. The process itself is designated in German "Das Darren," and I propose, for the sake of convenience, to name it the "Drying Process;" and the furnace, the "Drying Furnace."

DESCRIPTION OF THE DRYING FURNACE.

In old metallurgical treatises the best engravings of this furnace are, in my opinion, those of Schlüter,[8] and, in treatises of later date, those of Karsten.[9] A quaint woodcut of such a furnace is given by Agricola,[1] of which a reduced copy is annexed, fig. 59.

The furnace consists of a chamber of brick or stone work, rectangular in plan, closed at the back but open at the front, arched over at the top from side to side, and having a floor which slopes downwards from back to front. The side walls are vertical up to the springing of the arch, which commences at the height of several feet from the ground, and the back wall is vertical up to the top. Within this chamber, extending from front to back, is a series of low, parallel, vertical, straight walls of brick or stone work of equal height,

[8] Gründlicher Unterricht von Hütte-Werken, 1738. plate 50.
[9] System der Metallurgie. Atlas, plate 46. figs. 960, 961, 962, 963.
[1] De Re Metallicâ, 1561. p. 424.

and set at a certain and equal distance apart from each oth
secutively; and in the back wall there are openings into flu
responding to the spaces between these walls. In some furnac
of cast-iron, and even of copper, are laid longitudinally on th
of the walls, while in others they are left bare. The sloping
made either of brickwork, loam (a mixture of clay and sand), c
iron. The front of the furnace from the level of the tops of
walls upwards is closed by a sheet-iron door, strengthened
edges and cross-wise with bars of iron; the door is either l

Fig. 59. Drying furnace.

A. Foris demissa (door let down).
B. Contus (bar).
C. Panes fathiscentes (exhausted cakes).
D. Lateres (bricks).
E. Forceps (tongs).

or, as was more usual, suspended by a chain passing over a
and attached to a winch, or counterpoised lever; and it is s
with hooked bits of iron in order that the clay with whic
plastered over may stick firmly on. The spaces between t
walls (*Darrgassen*) are open, and serve the double purpose
places—wood being the fuel used—and receptacles for the li
molten product which drops from above. Furnaces diffe
dimensions, relative as well as absolute, and in minor detai
the construction of all, so far as I have been able to ascerta
essentially the same. In the engravings of this furnace

metallurgical treatises, the furnace is shown with a hood at the front, like that of a red-lead oven.

A drying furnace, such as was formerly in use at Neustadt, and was capable of holding 150 centners of the residual copper cakes, is shown in the annexed woodcuts, which are copies of the engravings numbered 960, 961, 962, 963, in the Atlas belonging to Karsten's "System der Metallurgie."

Fig. 60.

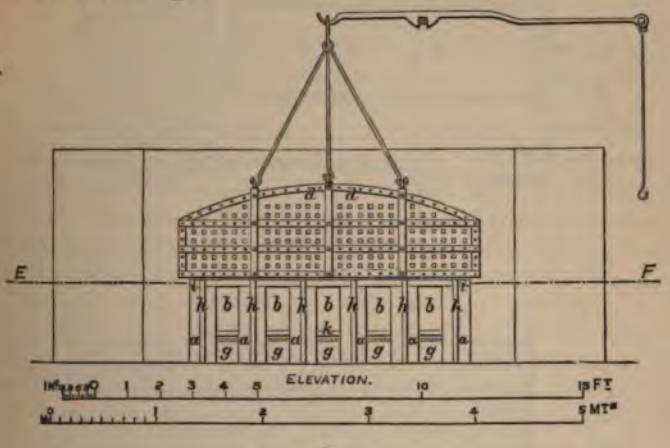
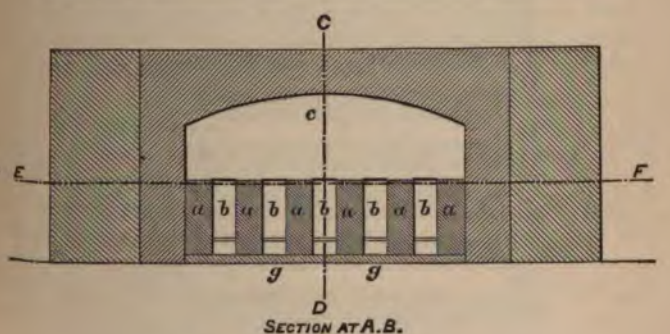


Fig. 61.

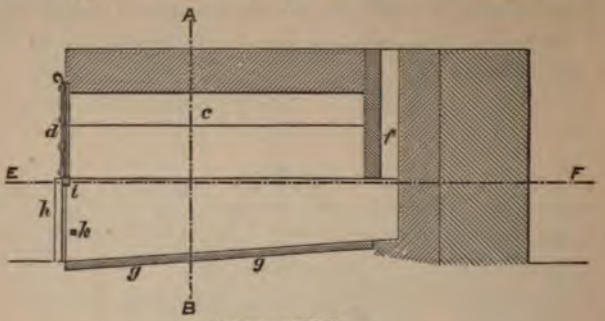


Figs. 60–63. Drying furnace at Neustadt.

a a. The walls (*Darrbänke*).
b b. The passages between the walls (*Darrgassen*).
c. Arched roof.
d d. Door, of sheet-iron, plastered over with clay on the inner side.
e. Lever for raising and lowering the door.
f f. Flues which communicate with the passages *b b*, and open into the chimney under which the whole furnace stands; these flues are provided with dampers.
g g. Cast-iron plates forming the floors of the passages *b b*, and sloping 7½″ from back to front.
h h. Iron standards for keeping up the walls, *a a*, in front.
i i. Strong iron bar, to serve as a fulcrum for the great iron crow-bars used for detaching the masses of residual copper (*Darrlinge*).
k. Smaller iron bar for supporting the tools used for drawing out the oxidized product (*Darrost*).

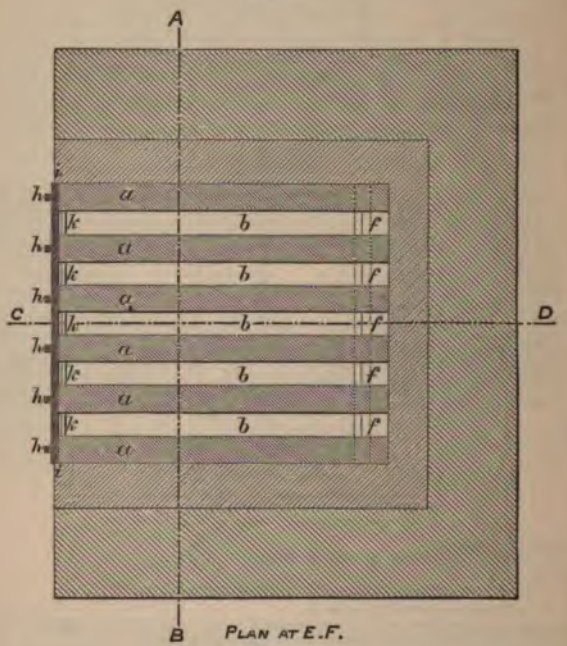
At Oker, what is called the Hungarian drying furnace was used, in which there is a fire-place on each side, extending from front to back, and with a grate suitable for the use of faggots. The object of this arrangement is simply to heat the furnace at the beginning of the process, after which firing is effected in the manner previously

described.[2] Cancrin suggests that in a furnace similar in constr to the Hungarian drying furnace, the three operations of le liquating, and drying may be conducted; but it is not whether his suggestion was ever put to the test of experiment.[3]



SECTION AT C.D.

Fig. 62.



PLAN AT E.F.

Fig. 63.

According to Karsten, the mistake is often made of incr the height of the furnace, in order that it may receive a larger charge than that of the Neustadt works, as much ev

[2] Kerl, Die Rammelsberger Hüttenprozesse, 1854. p. 109.

[3] Franz Ludw.v. Cancrin, Einrichtung und Gebrauch des von ihm beschriebenen Cupoloofens zum Frischen, Saige Darren, jedes mit Torf, Stein Wellen und Schertholz, 1791.

300 centners at a time. But he maintains that in such capacious furnaces the upper part does not become sufficiently heated, and that consequently the separation of the residual lead is less perfect there.[4] In some of the engravings in old metallurgical treatises drying furnaces with high-arched roofs are represented.

MODE OF CONDUCTING THE PROCESS.

The following description is mainly derived from Schlüter's treatise, and the rest from Karsten's "System der Metallurgie," and his paper in the first series of his "Archiv:"—

The low walls are plastered over with clay, to protect them, as far as possible, from the corrosive action of the oxidized product; and the liquated cakes are set in rows on the tops of the walls across the passages between them, precisely in the same manner as in the first liquation furnace, and with the same parts downwards, because the lower parts of the cakes are, as a rule, the least heated in the first liquation, and therefore the least liquated; whereas, in this second process, they are the most heated, and therefore the most liquated. It is essential to arrange the cakes with sufficient spaces between them to enable the flame from underneath to play freely around them. Hence, there should be only a single row of cakes, and the space between them and the roof should be filled with broken-up cakes, care being taken that these pieces also should be so piled as to obstruct as little as possible the passage of the flame. Moreover, this method of charging prevents the sintering together of the masses of copper, which sintering makes it extremely difficult to draw them out of the furnace after the process is ended. When the furnace is charged, the iron door is let down, and luted with clay at the sides and top; but, according to Schlüter, only so luted at the sides in order that some of the flame may escape from the top, and thereby heat the front of the furnace. A wood-fire is then made in the forepart of each of the passages between the low walls, all the draught-holes or flues being then open; the fire is gradually increased until the copper within the furnace becomes dull red-hot ("braunroth," brown-red, according to Schlüter). But it almost always happens that the copper at the back of the furnace becomes sooner red-hot than that at the front, owing to the flame being drawn in that direction by the flues, which it then becomes necessary to close, in greater or less degree, in order to drive the flame towards the front, and heat the copper uniformly throughout.

At first a little metallic lead trickles down, which is added to that obtained in the first liquation. When this trickling has ceased, but not sooner (Karsten), and the copper begins to "sweat," that is to yield oxidized product (*Darrost*),—which, for the sake of brevity, I will henceforth designate the slag,—the heat should not only not be increased, but may even be lowered, in order to let the coppery

[4] System der Metallurgie, v. p. 446.

masses shrink (*sich setzsen*).[5] Indeed, there is no harm in wholly withdrawing the fire for a short time; for when the temperature is too high, the copper readily melts and runs down into the spaces between the walls which support it. But after some molten slag has been formed, the copper better supports the stronger heat to which it is subjected towards the end of the process, in order to promote the formation of as much slag as possible so long as it continues "leady" (*bleyisch*) and holds silver; and the larger the quantity of lead separated, the shorter is the time needed afterwards to refine the copper, the less silver will the refined copper retain, and the greater will be the profit.

According to Karsten, the temperature is gradually raised by hal opening the flues, and prolonged for 14 or 15 hours. The slag which drops down, solidifies on the floor of the passages; whence i is dragged out, with long iron crooks or rabbles, every 2 or 2½ hours and immediately afterwards cooled with water. Special care should be taken to keep the passages quite free from slag; otherwise it is continually accumulating on their bottoms—particularly when they are not covered with cast-iron plates,—until it is no longer possible to keep the passages clear, especially when, towards the end of the process, the walls and the loam, with which they have been plastered over, are strongly attacked by the slag, which, in proportion to the silica and alumina abstracted by it from those parts, becomes less and less fusible. The substance formed by this action of the slag i designated in German "Darrsohle."

After the lapse of 15 hours, the interior of the furnace is quit red-hot; but the slag now appears more sparingly, because the lea has been liquated from the outer parts of the copper, and can only b replaced by that in the interior. As a certain time is required fo the lead to diffuse itself towards the exterior of the copper, raisin the temperature would not quicken liquation, and might cause th whole mass of copper to melt. It is, therefore, not expedient to rais the temperature higher than is necessary for such diffusion; and th best course, according to Karsten, is to prolong the firing gentl for about 4 hours, with closed flues, which suffices for that objec But at some liquation works this lowering of the temperature durin a certain period is not practised, and the temperature is continuall increased to the end of the process, not with the effect, it is asserte of rendering the liquation of the lead more complete, but only unnecessarily augmenting the consumption of fuel. In the secon stage of the process, with closed flues, little slag is formed, whic contains more oxide of lead and less oxide of copper than that pr duced in the first stage, or in the third stage now to be described. I this third stage the flues are again opened, and the process prolonge for about 8 hours at an increasing temperature. The slag drawn out of the passages every 1½ hour, or at least every 2 hour

[5] In Hellot's Translation it is "in order to give time to the copper shrink" (*s'affaisser*).

in order that as little as possible of the substance, previously mentioned under the name of "Darrsohle," may be formed. The longer the process lasts, the poorer becomes the slag in oxide of lead, and the richer in oxide of copper. Liquation is considered to be at an end when the slag becomes reddish in colour. If, however, the temperature be again somewhat lowered by closing the flues, and afterwards increased, lead in larger proportion would be extracted from the copper; but in that case there would be a further loss of copper, which would not be compensated by the increased yield of liquated lead.[6]

After the termination of the process, the door of the furnace is raised, and the masses of copper which have become sintered together are loosened with crowbars, then drawn out with iron hooks, while still red-hot,[7] and immediately plunged into water. But at some works the masses are left to cool within the furnace, which, with the door raised and the flues all open, requires two days. They come out coated with a glaze-like scale of oxide of copper and lead, termed "Pickschiefer" in German; and, as it contains silver in notable quantity, it is detached and reserved for further treatment. The detaching of it is effected by the slow and very tedious process of chipping with a hammer. By rapid cooling, however, much of the scale flies off, and the rest is thereby rendered more easily removable, for which reason rapid cooling is preferable to slow cooling.

The following remarks respecting the completion of the process are by Schlüter:—"When the work goes on properly, and no more slag drops down, but the copper begins to get teeth (*Zacken zu kriegen*), the fire is extinguished and the passages are thoroughly cleaned out; and what remains therein must, after the furnace has become cold, be completely drawn out." To "get teeth"—or, as it is translated in Hellot's edition of Schlüter, to "form points" (see p. 323 antea)—means, I infer, the running down of the copper into stalactite-like pieces, thus indicating incipient fusion. The drying process, according to Schlüter, requires from 20 to 24 hours for its completion, and double that time is needed to cool the furnace enough for the drawing out of the copper.[8]

The quantity of the products obtained in this process depends on the extent to which the copper has been liquated in the first operation, as well as in this. During many years at Neustadt, 100 centners of residual copper from the first liquation (*Kiehnstock*) yielded in this second liquation (*Darren*) 60 of copper residues (*Darrlinge*), 36·66 of oxidized product or slag (*Darrost*), 6·66 of scale of oxide of copper and lead (*Pickschiefer*), and 1·34 of the slaggy substance previously mentioned under the German name of "Darrsohle;" and the fuel consumed amounted to 200 cubic feet of common pine-wood (*Kiefernholz*). At the Hettstädt liquation works, where the original cakes were subjected to much stronger liquation than at Neustadt, and with

[6] Karsten, System der Metallurgie, 5. p. 449. The whole of this paragraph is extracted from Karsten's description.

[7] Archiv, 1st series, 9. p. 35

[8] Op. cit. p. 503

the production of three times as much "Saigerdörner," only 20 p cent. of slag (*Darrost*), but more than 4 per cent. of "Darrsohl were obtained.[3] But the following somewhat different results a reported by Karsten in his paper in the Archiv (1st series, 9. p. 3 —100 parts of copper residues from the first liquation proc (*Kiehnstöcke*) are stated usually to yield 66⅔ of the second copp residues (*Darrlinge*), 33⅓ of "Darrost," 5 of "Darrsohle," and 6⅔ "Pickschiefer;" but he considers this statement inaccurate.

PHYSICAL CHARACTERS AND CHEMICAL COMPOSITION OF THE PRODUCT OF THE DRYING PROCESS.

Residual Copper (*Darrling*).—A specimen in my collection fro Hettstädt is much more compact than the residual copper (*Kiehnstoc* from the first liquation process, is copper-coloured, and as though were glazed on the unfractured surface.

A specimen in my collection from the Rammelsberg is more or l cavernous, with globular cavities larger than peas, is copper-coloure and has a shining black glaze on the unfractured surface.

According to Karsten, this residual copper consists of 85 per cer of copper and 15 per cent. of lead; that is, about $\frac{1}{20}$ of the origin lead, provided the liquation cakes were composed of the usual pr portions of lead and copper, namely, 78·57 per cent. of lead a 21·43 per cent. of copper.[1]

The percentage composition of five different pieces of the residu copper (*Darrling*) was found by Karsten to be as follows:—

	I.	II.	III.	IV.	V.
Copper.....	82·7	85·6	83·4	87·2	90·6
Lead.....	17·3	14·4	16·3*	12·8	9·4

* The 3 is probably a typographical error, and should be 6.

The first four pieces were produced in one and the same operatio and the fifth was remarkable for its pure copper-red colour.[2] Fr the foregoing results it appears that the chemical composition this residual copper may vary considerably, even in the same furna charge; and such variation would seem to indicate that the char in a drying-furnace is not subjected throughout its mass to precise the same conditions of temperature, oxidizing action, etc., and th consequently this drying process, even on that account alone, is ve imperfect and unsatisfactory.

The lead in the residual copper (*Darrling*) is not equally diffus through the mass, but decreases from the centre towards the surfa so that a "Darrling" which has been badly liquated may be know by the pale red colour of the fracture of its central portion.[3]

Oxidized product or slag (*Darrost*).—A piece in my collection fr Hettstädt has the following characters:—Compact; the upper a unfractured surface is irregularly mammillated, as if formed by t successive droppings of molten slag, and is black and smooth; t fracture, perpendicular to the surface, is dull, somewhat crystalli

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[3] System der Metallurgie, 5. p. 450.
[1] Archiv, 1st series, 9. p. 14. [2] Idem, p. 36. [3] Idem, p. 40.

here and there, and dark brownish-red, and shows more or less of cleavage parallel to the surface, such as would result from the formation of the piece in successive layers; it does not apparently contain any unoxidized metal.

Another specimen in my collection from the Rammelsberg is slag-like, very uneven at the surface, porous, more largely crystalline than the preceding specimen, light reddish brown, very heavy, and contains unoxidized metal.

Its composition is very indeterminate: it contains, according to Karsten, from 70 to 85 per cent. of oxide of lead, from 4 to 8 per cent. of cuprous oxide, from 9 to 14 per cent. of silica, from 1 to 2 per cent. of alumina, and usually also about $\frac{1}{2}$ per cent. of ferrous oxide. The silica and alumina are derived from the materials of which the furnace is made. The slag may be regarded as consisting, for the most part, of silicate of protoxide of lead, with some silicate of dioxide of copper or cuprous oxide. (See the article on Silicates of Protoxide of Lead in the Author's volume on the Metallurgy of Lead, pp. 27 et seq.)

The following analyses of the oxidized product or "Darrost" were made by Karsten, and published in his "Archiv:"[4]—

	First Stage.			Second Stage.		Third Stage.		
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Oxide of lead (PbO) ..	84·2	78·5	76·50	79·8	85·1	81·2	78·9	77·1
Cuprous oxide	4·1	7·9	7·88	5·1	4·1	4·3	6·3	7·6
Ferrous oxide	0·4	0·5	0·50	0·4	0·3	0·3	0·5	0·3
Alumina	1·1	1·7	1·80	1·2	1·0	1·2	1·8	1·8
Silica	10·2	11·4	13·30	13·5	9·5	13·0	12·5	13·2
	100·0	100·0	99·98	100·0	100·0	100·0	100·0	100·0
Ratio between the copper and lead in 100 parts ... Lead..	95·55	91·22	91·03	94·23	95·60	95·17	92·91	91·38
Ratio between the copper and lead in 100 parts ... Copper	4·45	8·78	8·97	5·77	4·40	4·83	7·09	8·62

The specimens analysed were taken at intervals from the beginning to the end of one and the same operation, in which Karsten recognizes three stages,—namely, the first, which lasts from 8 to 10 hours, and during which the flues of the furnace are open; the second, which lasts from 3 to 4 hours, and during which the flues are partially or wholly closed (*bei gedämpften oder geschlossenen Zügen*); and the third and last stage, which lasts from 6 to 8 hours, and during which the flues are open.

The remarks which Karsten makes on the foregoing analyses are as follow:—Oxide of lead forms the greatest part of the "Darrost," and is present in the largest proportion in No. II. stage, when the

[4] 1st series, 9. pp. 36, 37.

flues are closed (but, as will be perceived, this statement is only correct with regard to the second specimen taken during that stage); and that this oxide from the beginning to the end of the first stage decreases in the same proportion as it does from the beginning to the end of the third or last stage. The quantity of cuprous oxide does not appear to be either directly or inversely proportionate to that of the oxide of lead (a statement which is hardly justified by the figures recorded in the table). The "Darrost" would be a pure compound of oxide of lead and cuprous oxide, if it did not come in contact with the walls and the loam or clay with which the walls and floors of the passages are coated, and exert a solvent action thereon. Hence Karsten infers that it would be very advantageous to make the walls (*Darrbänke*), as well as the floors of the passages, of cast-iron, and not of brickwork and clay.

"*Darrsohle*."—A specimen in my collection from Hettstädt is compact, and consists chiefly of unoxidized hard metal of a leaden colour: there is adherent to it a piece of red brick and some glassy dark-brown slag. According to Karsten, it contains never less than 70 per cent. of oxide of lead, and towards the last from 8 to 9 per cent. of cuprous oxide (Karsten). A technical distinction is made between "Darrsohle" and "Darrost," whereas the only difference is that the former is merely that part of the latter which has become attached to the floor of the passages, and is thereby rendered less pure.

"*Pickschiefer*."—A specimen in my collection from the Rammelsberg consists of small, angular, scaly fragments, some of which are black and others dark-brown, and of bits of copper-coloured metal; its powder is red, and it certainly does not contain black oxide of copper in sensible quantity. In Karsten's "System," it is stated to consist of about 60% of cuprous oxide, and 30% of oxide of lead;[6] but in his "Archiv"[7] it is described as a mechanical mixture of both oxide of copper, of oxide of lead, and of metallic copper, which, on quenching the residual copper (*Darrlinge*) in water, remains attached in the scales to the "Pickschiefer." But cupric oxide constitutes by far the largest proportion of this substance, and amounts to from 60 to 7[illegible] per cent.; and the quite pure "Pickschiefer," which is detached by quenching the "Darrlinge" in water, consists almost wholly of the oxide (?). The largest amount of lead was found in "Pickschiefer" which had been detached from the "Darrlinge" by picking or chiping, and amounted to 20·3 per cent.

TREATMENT OF THE RESIDUAL COPPER FROM THE DRYING PROCESS.

The copper is either directly refined by the old continental method, in small, generally circular, hearths, with the aid of a blast, or, before being thus refined, is subjected to a preliminary partial refining in a furnace like the old German cupellation furnace, this preliminary treatment being termed "Verblasen" in German.[8]

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[6] Karsten, Archiv, 1st series, 9. p. 35.
[7] 5. p. 450. 1st series, 9. p. 36.
[8] The process of copper-refining above mentioned, and the German cupellati[illegible]

In the refining of the copper residues (*Darrlinge*) from the second or drying process, a slag very rich in oxide of lead is necessarily produced. The four following analyses of this slag, taken at intervals during one and the same refining, are given by Karsten:[9]—

	I.	II.	III.	IV.
Oxide of lead (PbO)	67·4	62·1	54·8	51·7
Cuprous oxide	6·2	10·4	19·2	19·8
Ferrous oxide	1·0	1·1	1·2	1·2
Alumina	3·1	3·4	3·4	3·4
Silica	22·3	22·9	21·4	23·9
	100·0	99 9	100·0	100·0

No. I. was the first-formed slag; Nos. II. and III. were taken at two periods in the middle of the operation; and No. IV. at the end, after the blast had been shut off and the copper was considered to be refined (*gaar*). From the presence of so large a quantity of silica in the slag, it is clear that the oxides of lead and copper, which it contains, are, for the most part, in the state of silicates. Potash was sought for in the slag, but none was found. Karsten thinks it hardly possible to obtain copper quite free from lead by this method of refining, and states that many samples of the refined copper contain as much as $\frac{1}{2}$ per cent. of lead.

Most of the silver in the copper residues of the drying process (*Darrlinge*) is not removed along with the slag produced when they are subjected to the copper-refining process, but is left in the refined copper, and may therefore be regarded as lost.

IV. TREATMENT OF THE OXIDIZED AND ACCESSORY PRODUCTS.

The object of this treatment is the extraction from the oxidized products, which mainly consist of oxide of lead and cuprous oxide in variable proportions, of as much lead and copper as is economically possible. The subject is not a little complicated, and much has been written upon it by old as well as modern metallurgists; but it is not necessary to consider it at length in this volume, because it is really in great measure a part of the metallurgy of copper and lead, to which a portion of one of the Author's previous volumes and the whole of another have been devoted.

Besides the oxidized products which are peculiar to the liquation process, there is the litharge resulting from the cupellation of the liquated argentiferous coppery lead, and the slag consisting of oxide of lead and copper produced in refining the copper residues or "Darrlinge" from the second or drying process. These products may be treated in various ways: thus the litharge may be separately

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furnace, have been described in former volumes by the Author, and the description, therefore, need not be repeated here. See also p. 309 antea, where the "Verblasen" process is described.

[9] Archiv, 1st series, 9. p. 46.

reduced to the metallic state, or it may be used, wholly or in part, instead of metallic lead, in preparing the cakes of argentiferous copper and lead; while the slag from the refining of the "Darrlinge," which contains a large quantity of oxide of lead and a considerable quantity of oxide of copper, may be reduced, in a blast-furnace or otherwise, and the resulting mixture of metallic lead and copper passed directly through all the stages of the liquation process, or be used as a source of lead in the leading of fresh argentiferous copper, according as the relative proportions of copper and lead render it suitable for one of those purposes or the other.

According to Karsten, the usual mode of treating what I have named the accessory products, formed in the liquation process, is the following:—All such products from the operations of leading, liquating, cupelling, and drying are mixed together in the same proportions as they are formed in those operations and reduced by smelting in a suitable furnace, a blast-furnace being generally, if not always, used for that purpose. This smelting is termed "Das Krätz oder Dörner-Schmelzen." The slags from the copper-refining are treated either by themselves or in admixture with those from the "Krätz"-smelting; but, as may be supposed, the copper produced in either case is inferior in quality to that obtained from the refining of the copper residues of the drying process.

The metal reduced in "Krätz" and slag-smelting is cast into cakes of the same form and size as the original liquation cakes, which, notwithstanding they contain a great excess of lead in proportion to copper, are subjected to precisely the same series of operations as in the first liquation process. The lead which is liquated, being argentiferous, is used for leading fresh argentiferous copper; and the various accessory products are treated with a view to the economical extraction from them of lead, copper, and silver; so that in liquation works there is, so to speak, an endless series of what the Germans designate "repetition processes." The greatest skill is needed on the part of the smelter in determining how best to utilize the various accessory products with which he has to deal.

By way of example the following composition of a charge for "Krätz"-smelting is given:[1]—

	Centners.
I. Slags from the leading process (*Frischschlacke*)	65
II. Slags produced in the liquation of the cakes (*Saigerkrätze*)	88
III. Litharge (*Glätte*)	100
IV. Cupellation furnace bottoms (which consist of lime-marl impregnated with oxide of lead) (*Heerd*)	42
V. Furnace accretions, *i.e.* metalliferous matter which accumulates in, and adheres to, the interior of the furnaces, and which is detached from time to time (*Ofenbruch*)	5
VI. Copper scale, containing silver, from the drying process (*Pickschiefer*)	12
VII. Oxidized product (*Darrost*)	82

No flux is added.

[1] Karsten's Archiv, 1st series, 9. p. 56.

Nos. I. and VII. are certainly silicates; but the greater part of the charges consists only of oxidized mixtures. The lime in No. IV. should, according to theory, act beneficially by combining with the silica of the silicates in Nos. I. and VII., and setting free the oxides of lead and copper, and so favouring their reduction to the metallic state. But as, according to Karsten, silicates of lime are not fusible enough at the temperature of reduction in low blast-furnaces, they must be made so by adding the more fusible silicates of lead and cuprous oxide. He therefore suggests that in cases in which these silicates have to be reduced, the addition of iron finery slags and iron ores would be advantageous, by supplying oxide of iron whereby the oxides of lead and copper might be displaced from their combination with silica, with the formation of readily-fusible ferrous silicate. The circumstances above stated, Karsten thinks, account for the large quantity of oxide of lead left unreduced in the slag from "Krätz"-smelting. An average sample of such a slag from Neustadt had the following composition per cent.:—

Composition of Slag from "Krätz"-smelting.

Oxide of lead	34·8
Cuprous oxide	1·6
Ferrous oxide	5·6
Lime	3·1
Magnesia	0·9
Alumina	12·9
Silica	40·9
	99·8

The large quantity of lead which these slags contain renders it necessary to re-smelt them, and at some works they are smelted over again three, four, or more times, until, indeed, repetition ceased to be profitable. At the Neustadt works only two smeltings were needed, because coke was used for fuel instead of charcoal, whereby a higher temperature could be obtained than with charcoal; and at the same works, in the re-smelting of "Krätz" slags, 2 per cent. of cast-iron in small bits,[2] 8 per cent. of fluor-spar, and 8 per cent. of iron finery slags formed part of the charge. But even in the slag which was formed in the smelting of such a charge, Karsten found 4·12 per cent. of oxide of lead and 0·18 per cent. of cuprous oxide, which are equivalent to 3·82 of metallic lead and 0·16 of metallic copper.

Results of Liquation, exclusive of the operations subsequent to the Drying Process.

The results of Liquation, exclusive of the operations subsequent to the Drying Process, may be conveniently stated in the following manner, L and C representing lead and copper respectively:—

[2] "Wascheisen," *i.e.* particles of cast-iron obtained by stamping and washing iron-smelting furnace slags. Such economy as this may surprise an iron-master of modern times. See Idioticon der Österreichischen Berg- und Hüttensprache. Wien, 1856, p. 258.

Liquation cake.
L = 78·6 + C = 21·4

Lead separated.
L = 69·6 + C = 1·8

Residual copper (*Kienstock*).
L = 9 + C = 19·6

2nd residual copper (*Darrling*).
L = 3·4 + C = 19·2

Oxidized product (*Darrost*).
L = 5·6 + C = 0·4

LOSS OF METAL IN LIQUATION, AND COST OF THE PROCESS.

It is estimated by Karsten that, in a single liquation of arg tiferous copper, for 100 lbs. of desilverized copper, from 32 to 35 of the lead used in the process and from 5 to 6 lbs. of copper lost. The greatest loss occurs in the drying and copper-refi processes.

In the whole series of operations, for 100 parts by weigh argentiferous copper, there are produced about 150 parts of which is thrown away as worthless. In this slag, however, t are 5·75 parts of lead and 0·25 of copper, which are lost. The by what is termed "burning" (*verbrennen*) amounts to 26·25 par lead and 4·75 of copper. The silver lost is partly in the ref copper, partly in the slags, and partly in the lead "burnt" away.

In the liquation of the black-copper produced at the Lauten Altenau, and Andreasberg smelting-works, Upper Harz,[3] the ave of loss in metal, during the years 1857–58, 1858–9, aud 1859 amounted to 25 per cent. of the silver, 25·1 per cent. of the and 9·3 per cent. of the copper. Hence the loss of lead per cen of black-copper operated upon amounted to 36·37 pounds, exclu of the lead existing in the black-copper. The costs of liquation centner of black-copper, during the above period, were as follow:

	Th.	ngr.	pf.		s.	d.
Labour	0	25	2	.....	2	6¼
Materials	1	26	8	.....	5	8½
Total.....	2	22	0	.....	8	2⅜

The cost therefore per ton was £8 6*s.* 6*d.*

[3] Berg- und Hüttenmännische Zeitung, 1864. p. 254.

Localities where Liquation was conducted.	For every 100 Ctr.* of black copper are produced:			Fuel per Ctr. black copper.		Labour for each liquation cake.	Yields from 100 Ctr. of liquation cakes.			Fuel per Ctr. of liquation cakes.		Labour for liquating 1 cake (325 lbs.).	Labour per Ctr. of residual copper yield:		Fuel per Ctr. of residual copper.		Labour in drying 1 Ctr. of residual copper.	Labour per Ctr. of "Darrlinge" or residual copper yield:		Fuel per Ctr. of "Darrling" or residual copper.		Labour for partial refining 1 Ctr. of "Darrlinge" or residual copper.	Refined copper from 100 of partially refined copper.	Fuel per Ctr. of part. refined copper.	Labour per Ctr. of partially refined copper.
	Liquation cakes or "Frischstücke." Ctr.	Slag. Ctr.	Waste. Ctr.	Charcoal. Cub. ft.†	Coke. Cub. ft.		Residual Copper or "Kienstöcke." Ctr.	Lead. Ctr.	"Saigerdörner." Ctr.	Charcoal. Cub. ft.	Wood. Cub. ft.		"Darrlinge." Ctr.	Lead. Ctr.	Charcoal. Cub. ft.	Wood. Cub. ft.		Partially refined copper. Ctr.	Slag. Ctr.	Faggots.	Charcoal. Cub. ft.			Charcoal. Cub. ft.	
						Ngr.‡						Ngr.					Ngr.					Ngr.			Ngr.
Oker, Lower Harz	240 R.[1] 200 P.[2] 440	14	3	7·75	0·48	..	30	P.[2] 29 R.[1] 25	17	1·66	0·44	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Lautenthal (Upper Harz)	.. ..	..	..	7·10	..	2·8	37	38	..	0·82	.. ..	..	89	7	5	2·94	0·5	..	.	..	..	..	..	..	..
Andreasberg „	350	..	..	..	..	..	31	38	..	?	.. ..	..	76	?	..	1·84	..	73[5]	?	17	..	1·7	85	7·7	8
Altenau „	325	17	..	11·66	..	..	25	37	34	1·31	Faggots 2½	1·0	..	..	..	..	..	55[4]	45	13	0·36	1·7	91	9·8	..
Neustadt-on-Dosse, Prussia	.. ..	..	..	..	..	..	29 25	64 57	4 15	9·95 ..	0·36	..	60 ..	.. ..	.. ..	2·00 ..	..	.. ..	.. ..	.. ..	.. ..	.. ..	..	.. ..	.. ..

[1] R. abbreviation for rich. [2] P. abbreviation for poor. [3] From "Darrlinge." [4] From residual copper.

* Ctr. = Centner. 1 Ctr. at Laut., Andr., and Alt. = 100 lbs. = 110·232 lbs. English (Avoirdupois).
1 „ Neustadt and Oker = 100 „ = 103·111 „ „ „

† 1 cub. ft. at Laut., Andr., Alt., and Oker = 0·88014 cub. ft. English.
1 „ Neustadt = 1·09184 „ „

‡ 1 Ngr. = about 1*d*.

CHARGES:—

1. *Leading* or "*Frischen.*"—At Oker, in one shift of 10–12 hours 5½·6 Ctr. of black copper are treated. For every 80 lbs. of granulated black copper:
   120 lbs. of litharge, 76–88 per cent. of lead, ½ Lth. silver.
   125 „ lead ½ „
2. *Liquation* or "*Saigern.*"—Charge 6–7 cakes, made in 4–6 hours.
3. *Drying* or "*Darren.*"—Charge 30–40 Ctr. residual copper in 10–12 hours.
4. *Partial refining* or "*Verblasen.*"—Charge 40 Ctr. "Darrlinge" in 10–16 hours. At Altenau, where the drying process is omitted.—Charge 40 Ctr. residual copper in 20–24 hours.
5. *Refining* or "*Gaarmachen.*"—Charge 2½–3 Ctr. in 4–7 hours.
6. *Treatment of the oxidized products* or "*Krätzfrischen.*"—"Saiger-," "Darr-" and "Gaarkrätz," also "Darr-" and refinery slag, are smelted with litharge, etc., and the resulting mixture of metallic lead and copper is liquated or used in the leading process.

Kerl, Hüttenkunde, 1855. 3. pp. 125 et seq.
„ Oberharzer Hüttenprozesse, 1860. pp. 643 et seq.
Karsten, System der Metallurgie, 5. pp. 427 et seq.

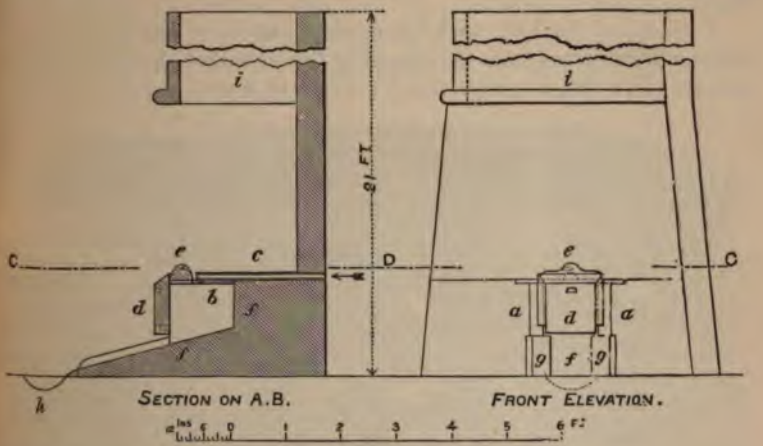
LIQUATION OF ARGENTIFEROUS COPPER IN JAPAN.

For the following description of the process of liquating argentiferous copper now in use in Japan, and for drawings illustrative of it, both by himself and by a native draughtsman, I am indebted to my friend Mr. J. H. Godfrey, lately Mining Engineer-in-Chief to the Imperial Government of Japan, who saw the process in operation at Kagoyama, province of Ugo; and to my friend Mr. C. Tookey, formerly Chief Assayer at the Japanese Mint at Osaka, I am indebted for a series of specimens illustrative of the process, which he saw practised at the Government Copper Works there, and of which he has likewise favoured me with an account. The first-named works, visited by Mr. Godfrey, belonged to the local municipal authorities of the district, and were wholly devoted to the liquation of argentiferous copper; but recently they have passed into the hands of the Imperial Government. Mr. Godfrey informs me that when he inspected these works they appeared to him to be conducted in a very satisfactory and businesslike manner.

The unrefined argentiferous copper, or black-copper, which is the subject of treatment, is produced in the smelting of argentiferous copper ores, and yields by liquation, on the average, 0·114 per cent. of silver, *i.e.* about 37 ounces per ton. It is broken by hand into pieces of about the size of the fist, and then melted with the addition of metallic lead in the usual little Japanese blast-furnace or hearth, which consists merely of a circular cavity made in the ground, and brasqued with a mixture of clay and charcoal-dust duly moistened with water. There is only one twyer, and the blast is produced by means of a wooden rectangular blowing machine similar to what is used in China, and is described in the Author's volume on Iron and Steel. A charge is composed of 267 lbs. (Avoirdupois) of black-copper and 50 lbs. of lead. The copper is first put in, and the lead is not added until the charcoal in the furnace has become well ignited throughout. The molten metal is taken out of the hearth in successive portions by means of a cold iron bar, enlarged at one end into a globular knob as shown in the woodcut on page 342. The large end of the bar is dipped into the metal, which, where it comes in contact with the cold iron, solidifies and forms an adherent crust. The bar is now removed, its encrusted end plunged into water, and the crust knocked off with a hammer; and this manipulation is repeated until nearly the whole of the metal has been removed from the hearth. The crust is broken into small pieces, and in this state subjected to liquation. According to Mr. Tookey, the practice at the Osaka Mint was to knock off the crust while hot and easily frangible, and then to quench the pieces in water; the knocking off was effected by simply striking the encrusted end against the floor. Six charges, composed as above stated, are melted daily in one furnace, with a consumption of 410 lbs. of charcoal. At two of these "leading" furnaces, five coolies, labourers, are employed.

Liquation is effected in a small blast-furnace, of which the co

struction is shown in the annexed woodcut. The weight of a charge for one liquation is 116 lbs. Any slag from the last liquation, which may adhere to the hearth, having been removed, the furnace is charged in the following manner. The largest pieces of the mixture of copper and lead are placed on the bottom, some charcoal over them, the smaller pieces upon the charcoal, and lastly ignited charcoal at the top; after which the furnace is closed and the blast let on. As soon as the lead begins to flow, and a pasty mass protrudes from under the cover, this mass is squeezed back with a wooden stick



a a. Two flat stones forming the side-walls.
b. A large brick, 1 in. thick, covering the top of the furnace.
c. Blast-pipe of wrought-iron, semicircular, placed with its flat side downwards, 2 in. in diameter, with an elbow underneath, at the furnace end, in order that the blast may be deflected downwards; the elbow is ¼ in. by 2 in., inside measure.
d. Movable brick for closing the front of the furnace.
e. Movable brick, for closing the opening at the top of the furnace. This brick, and also the preceding one, are, at the time of working, kept in their places by propping them with some of the iron tools used in the operation.
f f. Floor and back-wall, lined with brasque.
g g. Two stones, between which is a floor of brasque, with a gutter cut in it along the median line.
h. Brasqued cavity for receiving the liquated lead.
i. Hood, for carrying off the fumes and furnace gases, which is made of strips of bamboo covered with loam.

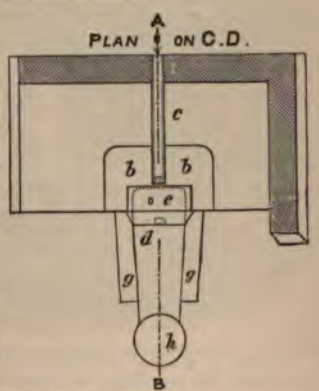


Fig. 64. Description of Japanese liquation furnace.

fastened to an iron hook; and when the mass has become too hard to yield to the stick, it is thrust back with an iron rabble, so that it may be re-heated sufficiently to render it again pasty. As soon as this occurs, the wooden stick is used as in the first instance, and this kind of manipulation is repeated until lead ceases to trickle out. A charge of 116 lbs. is liquated in three hours, with a consumption of 52½ lbs. of charcoal. A man and a woman are employed at each of these liquation furnaces.

The products of the liquation of a charge of 116 lbs. of the mixture of copper and lead are as follow:—

Lead (containing 0·65 per cent. of silver, or 212 ozs. 6 dwts. 16 grs. per ton)	16 lbs.
Copper residue	94½ „
Slag	6 „
"Saigerdörner," for which the Japanese name is "Shirome"	1¼ „

But if the operation is properly conducted, no "Shirome" is produced.

Supposing the lead used for mixing had been non-argentiferous, the silver extracted from the copper in the liquation charge of 116 lbs., namely 97·71 lbs., amounts to 1 oz. 10 dwts. 8 grs., say 1½ oz.

Fig. 65. Workmen in the Government Copper Works at Osaka, Japan, from a photograph taken by Mr. C. Tookey. The globular-ended bar employed in liquation is held by the central figure. The crucibles are such as are used in the melting of copper.

The proportions of silver in the various specimens illustrative of the Japanese Liquation Process, which I received from Mr. Tookey, have been determined by R. Smith in the metallurgical laboratory of the Royal School of Mines, and the results are as follow:—

	Per cent.		Silver. Per ton. ozs.	dwts.	grs.
Argentiferous copper (*Arado*)	0·1133	...	36	19	20
Lead added to the copper (*Aranamari*)	0·0746	...	24	7	9
Liquated lead (*Denamari*)	0·54	...	176	8	0

The silver (*Dehaifukigin*) extracted contained 0·21% of gold and 0·45% of copper.

In fig. 65 is shown the bar with a globular end mentioned in the foregoing description. The bar is held by the central figure.

TREATMENT OF CUPRIFEROUS LEAD CONTAINING SILVER AT LEAD-SMELTING WORKS IN FLINTSHIRE, NORTH WALES.

For the following practical observations on this subject I am indebted to my excellent friend Mr. Allan Dick. He states that he has had great personal experience in the treatment of mixed ores and furnace products, which contained lead, copper, and silver.

The mixture of ores or furnace products, yielding lead and copper, is smelted either in a small blast-furnace or in the flowing-furnace,[4] and tapped, as usual, into the lead-pot, the slag running out at the same time; but if "slurry" (a local name for regulus) be formed, it will contain the bulk of the copper. The metal under the slag in the lead-pot, and while still very hot, appears to be perfectly homogeneous. When some of it is taken out in a ladle and poured back into the lead-pot, it runs like mercury; and the surface of the metal in the lead-pot is smooth. As the temperature falls, a coppery alloy rises to the top; and when in this state the metal is poured from a ladle, it runs thick like the mixture of crystallized and liquid lead in a Pattinson pot, and the surface of the metal in the lead-pot is rough. If left at rest, the surface of the metal becomes solid; and by thrusting a crow-bar through the crust of solidified metal, it will be found that this crust varies in thickness according to the proportion of copper in the lead. The crust can be broken up, and taken out with a perforated ladle, just as broken-up ice can be taken out of a frozen pond for removal to an ice-house; and, accordingly, if there be a sufficient quantity of this crust, it is so removed. The argentiferous lead in the lead-pot, after the extraction of the crust, may, *while still very hot*, retain about 0·5 per cent. of copper: it is laded into ingot-moulds and reserved for further treatment. During cooling, more copper is thrown out, so that when the lead is re-melted in a large pot, say capacious enough to hold 10 tons, nearly the whole of the copper comes to the surface; it does not, however, form a cake, or float like oil on water, but is a frothy scum, more like yeast on the surface of beer. This scum is skimmed off as far as practicable, and may be mixed with the skimmings from the lead-pot. The skimmed lead may retain about 60 ozs. of copper to the ton; and, if pattinsonized, a coppery skimming will be obtained, which may be added to the previous skimmings. But as such lead does not pattinsonize well, it is generally "improved," *i.e.* passed through a softening furnace, before it is pattinsonized;[5] for only tolerably pure lead pattinsonizes well. Although copper is

[4] For a description of the flowing-furnace, and the mode of conducting the process of smelting therein, the reader is referred to the Author's volume on the Metallurgy of Lead, pp. 257 et seq.

[5] See the Author's volume on the Metallurgy of Lead, pp. 458 et seq.

not a great hindrance in this desilverizing process, yet it is better to extract nearly all the copper from the lead operated upon. Zinc, however, is a greater hindrance than copper, and if present in the lead to the extent of only a few tenths per cent. reverses the results of pattinsonization in poor lead containing, say, 4 or 5 ozs. of silver per ton; the bulk of the silver, instead of remaining in the liquid lead or "bottoms," then passing into the crystals through the action of the zinc, as in Parkes' process of desilverizing lead by zinc. The reason is, therefore, evident; but copper appears to act in another way, namely, by making the crystals very small and difficult to drain.

The coppery skimmings are "sweated," *i.e.* liquated, on the bed of a reverberatory furnace. The bed is made red-hot and then spread over with small coal to the depth of an inch or two. As soon as the coal is coked, the skimmings are thrown into the furnace, and the lead which "sweats" out is laded into ingot-moulds as usual, after which the coppery residue is withdrawn from the furnace. This residue consists of a mixture of metallic copper and lead, oxides of copper and lead, and cinders: it is generally treated in the flowing-furnace along with "slurry" or "slurry-yielding" materials, and the product is sold to copper-smelters.

In the smelting of ores and mixtures, the lead-smelter tries to avoid making this very coppery lead by so composing the charge as to cause some "slurry" from each charge to take up the bulk of the copper; but, of course, that is not always practicable.

Reich has investigated the liquation of cupriferous lead under conditions similar to those above stated, and has published the following observations on the subject,[6] which are quoted in the Author's volume on the Metallurgy of Lead (pp. 91, 92). When cupriferous lead is melted at the lowest possible temperature, and the unmelted or half-melted substance, termed "Abzug," floating on the surface, is removed, this "Abzug" will contain most copper, and the residual lead will be proportionately poor in copper. But when the temperature is raised and the "Abzug" is not removed, the proportion of copper in the lead rapidly increases with the temperature. Unrefined soft lead was slowly melted in a refining furnace (*i.e.* the German cupellation furnace) by gradually raising the temperature, and after the lapse of two hours, when it had scarcely reached incipient redness, the "Abzug" was taken off. The subjacent lead contained 0·08 per cent. of copper, while the "Abzug," which was wholly in the metallic state and rich in lead, contained 5 per cent. of copper. A portion of this "Abzug" was melted in a porcelain crucible, for which nearly a red-heat was required; and on the surface appeared a pulverulent and partially oxidized mass, which contained 20 per cent. of copper, while the subjacent lead contained only 0·4 per cent. Lead containing 0·974 per cent. of copper was melted at a moderate heat in a porcelain crucible, and yielded unmelted "Abzug," which contained 14·84 per cent. of copper. The conclusion, therefore, from

[6] Jahrbuch für den Berg- und Hüttenmann.; Freiberg, 1860. p. 186.

preceding statement is, that when cupriferous lead is liquated he manner described, the proportion of copper in the lead rated is greatly influenced by the temperature; or, what is valent to this conclusion, the solubility of copper in molten increases with the temperature.

Reich's results, it will be perceived, agree perfectly with those of ck; and they are analogous to what occurs in the case of silver d mercury, with this difference, that in the latter case it is rtainly a definite alloy of silver and mercury that dissolves in ercury, whereas in the former case it is not proved that there is ny such definite alloy of copper and lead.

Nevill's Method of Liquating Argentiferous Copper.

A patent was granted in 1843 to Richard Janion Nevill, of Llangennech, Carmarthen, for a modification of the liquation process.[7] Argentiferous copper, whether unrefined or refined, is melted and poured into a vessel of cast-iron or other suitable material, containing molten lead heated to redness or nearly so; and the two metals are well intermixed. On cooling, coppery metal containing lead and silver rises to the top, and, when sufficiently cool, is taken off with tongs or otherwise, or by drawing up a circular iron plate, with holes through it, and of nearly the same diameter as the mixing vessel, placed at or near the bottom of this vessel before pouring in the copper. The coppery metal so removed is broken into small pieces and heated in retorts, by preference of cast-iron, from 2′ 6″ to 3′ long and about 6″ square, which are fixed in a sloping position in a furnace, and are fitted with a cover at the lower end, having a small hole in or near the bottom. Charcoal or other carbonaceous matter is put into the retorts along with the pieces of coppery metal, after which the upper ends of the retorts are closed, in order to prevent the entrance of air. Heat is applied and gradually increased; and the argentiferous lead, which separates, flows into pans placed under the lower ends of the retorts to receive it. The silver is obtained from this liquated metal by cupellation.

Mr. Nevill was a member of the well-known copper and lead-smelting firm at Llanelly, not far from Swansea; and as he died many years ago, I applied to Mr. Charles Nevill, his son, and a member of the same firm, for information respecting this process; and am indebted to him for the following particulars. The process of liquation has been long abandoned at these works, but was thus practised there: "The unrefined [argentiferous] copper was melted in a small furnace, and the lead at a red-heat in a cast-iron pot. About 7 lbs. of the copper were taken out of the furnace in an

[7] A.D. 1842, October 18, No. 9909. The patent is, as was usual in those days, very comprehensive; its title being, "An improved method of separating certain metals, when in certain states of combination with each other." Abridgments of the Specifications relating to Metals and Alloys (excepting Iron and Steel), 1861, p. 119. A description of this method appeared in the Chemical Gazette, 1844. 2. p. 335, and of that description I have chiefly availed myself in the text.

ordinary 28-lb. ladle, and to this were added about 20 lbs. of the red-hot lead. The full ladle of the mixture was then emptied into a cast-iron mould, and obtained in the form of a strip about 2′ long, $4\frac{1}{2}$″ broad, and 1″ thick. The strips were placed in a close oven 5′ long and 2′ wide, the bottom of which was made of sloping plates of cast-iron provided with narrow gutters, and the roof of ordinary fire-brick. The strips were covered with carbonaceous matter, and over this oven played the flame from the fire-place from one end of the oven to the other. The process required about 10 hours. The coppery residue was re-melted, cast again into strips, and subjected to the liquation process a second time, without any further addition of lead. The lead was desilverized by the ordinary process, and the desilverized copper was returned to the copper-works." [February 1878.] From the foregoing description it will be seen that the process actually practised differed much from that prescribed in the specification of the patent above mentioned.

Liquation of Copper containing Gold.

Schlüter states that, having detected gold in a parcel of copper from Holland, by an assay on the small scale, he subjected the copper to liquation with lead in the same manner as in the liquation of copper containing silver, but found only a small portion of the gold in the liquated lead; and he ascertained by various experiments that the gold had, for the most part, remained in the residual copper, notwithstanding he had used much lead in the leading process. He reports that the copper upon which he operated was alloyed with as much as 50 per cent. of lead, and had been cast in the form of roun cakes and long pigs, varying in weight from less than 50 lbs. t 60 lbs. Some of the ingots contained more than half an ounce of go and a mark of silver per centner, while others only contained a dra of gold and an ounce or two of silver. The proportion of coppe which was pretty equal in all the ingots, amounted to about 62 lb of refined copper per centner; and Schlüter adds that the assa produce in gold and silver was so different that the assay of the t and bottom of an ingot rarely agreed with each other; so that it w necessary to take an average of the assays of the top and bottom a assort the ingots accordingly. He then gives a detailed account his experiments upon these ingots. From the copper, richest in go and silver, he extracted the whole of the gold and silver by refini (*i.e.* cupelling) it along with liquated argentiferous lead. But as t treatment was very costly, it could not be profitably applied to t poorest ingots, which contained only from three to four ounces of fi gold and silver, and which, therefore, were subjected to liquation wi the addition of much lead, *i.e.* in the proportion of 3 centners to 75 l of the copper, which originally was alloyed with nearly 50 per ce of lead. The liquated lead was refined in charges of 64 centners a time, along with 8 centners of copper rich in gold; but not much v gained by such refining, and the greater part of this rich copper v

refined with lead reduced from litharge and refining furnace bottoms, with the addition of the necessary quantity of fresh lead. The poorest copper, which yielded by assay only 2 ozs. of auriferous silver per quintal, was leaded by melting it conjointly with litharge and refining furnace bottom, in low blast-furnaces in the manner described in the early part of the preceding article on Liquation. But when the cakes thus obtained were liquated, only a small portion of the gold was found to have passed into the lead.

Notwithstanding the foregoing statements of Schlüter, Biringuccio asserts that gold as well as silver may be separated from copper by the old method of liquation with lead;[1] but in the French translation of Schlüter, edited by Hellot, there is no notice of that assertion, though Hellot had a fine copy of Biringuccio's treatise, which is now in my possession, and which contains his autograph.

Theoretical Considerations concerning the Liquation of Argentiferous Copper.

In the article on Assaying in this volume it is stated (p. 268) that the cornet of gold obtained by parting with nitric acid is much reduced in volume by annealing at a red-heat. This reduction in volume is due to the attraction of cohesion amongst the particles of gold, which takes place at that temperature. But the cornet, after annealing, remains a porous mass, the pores being in intercommunication throughout; and, without the application of an external compressing force, it would continue more or less porous at any higher temperature below the actual melting-point of gold. Now, suppose the pores of the cornet, before annealing, to be filled with a substance which is not volatilizable, has a much lower melting-point than gold, and exerts *no action* whatever upon gold at any temperature, it is clear that that substance would only be partially extruded by heating the cornet to any degree short of the actual melting-point of gold. Extrusion of the intermixed substance could only occur to the extent of the reduction in volume of the gold produced by the exercise of the force of attraction of cohesion amongst its particles; and at the temperature of incipient fusion that force becomes very feeble. But until actually melted, the gold would remain porous, and retain more or less of the intermixed substance; but at a certain temperature approaching its melting-point, the force of cohesion amongst its particles would be too feeble to cause further contraction of its mass, and that temperature determines the degree to which liquation can be carried.

In the process of puddling pig-iron, a ball, as it is termed, is obtained, which consists of a sponge-like mass of malleable iron infiltrated throughout with a slag of ferrous silicate, which has a much lower melting-point than iron, and which has no action at any temperature upon iron. In order to expel this slag and produce

[1] De la Pirotechnia, 1540, folio 53.

a mass of solid iron, the ball, while heated to a degree much beyond the melting-point of the slag but below that of iron, has to be powerfully compressed by mechanical means; but even by such treatment it is not possible wholly to separate the slag, though the particles of iron are at a welding-heat, and there is no sensible, or at least no considerable, adhesive action between the iron and the slag.

Now, let it be assumed that there is no chemical or solvent action between lead and copper at any temperature, and that, although they may be most intimately mixed by melting them together and stirring the molten mass, this mass is only a mechanical mixture; such, for example, as an emulsion or intimate mixture of oil and water. The mass after solidification will remain only a mechanical mixture of lead and copper. On heating such a mass to or beyond the melting-point of lead, but below that of copper, the lead, as we have seen, is partially liquated; and even when the mixture is composed of those proportions of lead and copper which long experience has shown to be the most favourable for the separation of the lead, yet a large quantity of lead always remains in the copper after liquation; and, according to the assumption that there is no chemical or solvent action between lead and copper at any temperature, such a result is precisely what might have been expected, and is in perfect accordance with what occurs in the case of the puddled ball.

The following remarks by Berthier on this subject appear to me to be well founded:—"When once a substance has been introduced between the molecules of another substance, it seems to me that we ought not to be astonished at finding that we cannot wholly separate it by bringing it into the liquid state; rather the contrary ought to surprise us: the liquid lead is retained by adhesion between the pores of the copper as water is in a wet sponge. If we exposed to a temperature above zero (*i.e.* centigrade, or the freezing-point of water) a sponge wholly penetrated with ice, much water would flow from it; but there would remain a certain quantity which we should not be able completely to separate, even by compression, and which would only yield to the evaporating power of heat."[2]

But, contrary to what has been assumed, there is chemical or solvent action between lead and copper at certain temperatures; and the question, therefore, arises whether this action affects the preceding considerations relating to the liquation of a mass of lead and copper and if so, how and to what extent.

From what has been advanced concerning the separation of lead from metallic copper by the liquation process, it may be concluded that molten lead has the power of holding a certain quantity of copper in combination or solution, and that this quantity increases with the temperature; and that, by causing the lead to cool very slowly without disturbing it, nearly the whole of the copper separates and rises to the surface (see p. 343). But whether the state in

[2] Annales des Mines, 1825. 11. p. 470.

which the copper exists in the molten lead be solution, combination, or both, remains to be decided.

That the copper is present in the molten lead in a state merely of mechanical suspension and diffusion, seems to be inconsistent with the facts that the proportion of copper in the lead, which trickles from the liquation furnace, and of which the temperature may be presumed to be pretty constant, is, as Karsten proved, remarkably constant, amounting on the average to 2·5 per cent. of the liquated metal (see p. 322); that the proportion increases with the temperature of the molten lead, as shown by the observations of Reich and Dick (pp. 343 and 344); and that when a thin sheet of copper remains immersed for a comparatively short time in molten lead kept just about the melting-point of lead, it is partially dissolved and attacked in such a manner as might be expected from the action of a solvent, in proof of which the following experiment is presented. A piece of cleaned thin sheet-copper was immersed in lead kept molten just above its melting-point; but the lead did not appear to dissolve any of the copper, to which particles of lead here and there adhered. The experiment was repeated with a fresh piece of similar sheet-copper, the surface of the molten lead being covered with rosin, when, after the lapse of two hours, a hole, with rough edges, was observed in the copper. Further evidence to the same effect —namely, that the copper does not exist in molten lead in a state merely of mechanical suspension and diffusion—will now be presented.

In the volume which I have published on the Metallurgy of Lead (p. 92), a detailed account is given of the change which an ingot, consisting of 1 part of argentiferous copper and 3 parts of lead, by weight, underwent in the course of 23 years, atmospheric air having had access to the ingot during the whole of that period. It was acted upon to a considerable depth, and became encrusted with a brown substance of the following composition per cent.:—

Lead	81·59
Copper	9·48
Silver	0·78
Oxygen	6·28
Carbonic acid	1·47
Water	0·32
	99·92

On boiling this brown substance with an aqueous solution of caustic potash, insoluble matter was left, which, when magnified from 50 to 100 diameters, was found to consist of bright crystals, resembling metallic copper, many of which were aggregated in radiated clusters. Now, admitting that these crystals were copper, as I think we may without much risk of error, the question occurs, whether they originally existed in the ingot or whether they were produced after it had been cast and solidified. There is strong positive evidence, I think, in favour of the first view, to say nothing as to the difficulty

of conceiving how, supposing the solidified ingot to have originally been absolutely homogeneous, crystals of copper should have been formed in it afterwards, under the conditions mentioned, one of which is that it had not been heated beyond ordinary atmospheric temperatures.

The following experiments, made in my laboratory in 1877, tend to throw light on the question under consideration. To 15321 grs. of molten lead heated in a plumbago crucible to strong redness 5107 grs. of cold copper were added; and the mixture was further heated to bright-whiteness, when it was stirred with charcoal, which caused violent action, attended with the projection of some of the metal from the crucible. After placing pieces of charcoal over the metal, the crucible was closed with a cover, and left to cool as slowly as practicable during about 36 hours; with which object the furnace was filled with coke-dust and anthracite in small lumps at the top, the damper was let down, the ash-pit register door shut, and the cover of the furnace so set that a little air might pass directly into the flue near the top. The lump of metal thus obtained was somewhat concave on the top, and consisted of two distinct layers. The upper layer was about $\frac{1}{4}''$ thick, and copper-red on the surface; but when cut through, or scraped with a knife, it acquired a lead-like colour, which, on exposure to the air, again became copper-coloured. There was a sharp line of demarcation between this and the lower layer, which was about $1\frac{3}{4}''$, and resembled lead in colour; the external surface of this layer was highly crystalline, and portions of it when seen under the microscope showed small bright copper-red perfect octahedra. The upper layer contained 68·86%, and the bottom of the lower one 7·43% of copper.

In another experiment 11403 grains of molten lead were gradually poured into molten copper, and the whole was well stirred with a piece of wood, which caused some loss of metal by projection. After placing bits of charcoal over the molten mixture, the crucible containing it was covered and treated as in the preceding experiment. The lump of metal thus obtained was similar to that produced in the preceding experiment.

The separation of copper in a crystalline form from a molten mass of lead and copper, which has been slowly cooled, is perfectly consistent with the view that the copper was present in that mass, to a considerable extent at least, in a state of actual solution, but is not consistent with any other view, except, perhaps, that of chemical combination, to which, however, the results of Reich's experiments (see p. 344) are unfavourable. Yet there are cases in which one body seems to exist in combination with another body while the latter is molten, and to separate wholly or partially during subsequent solidification. The following examples of such cases may here be mentioned. Phosphorus is taken up in considerable quantity by molten lead or silver, but is nearly completely evolved during solidification. Carbon is separated in the state of graphite from molten grey pig-iron during solidification; and when cooling is very slowly effected,

the separation is nearly complete. But it may be argued that these are cases of solution, and not of chemical combination. With respect to phosphorus, I can adduce no direct evidence as to its mode of existence in molten lead or silver: it may be solution, or it may be chemical combination; it must be one or the other, or both. With regard to carbon, there is evidence that it may exist in molten pig-iron, both in the state of solution and chemical combination. But there is another case in which it is certain that one body exists in another body in a state of chemical combination, but only while the latter is molten, and separates during solidification; namely, the case of the regulus produced in copper-smelting, which is called "blue-metal," and which is composed of copper, iron, and sulphur. This regulus always contains fine and more or less filamentous particles of metallic copper diffused throughout the mass, not *globular* as they would be, if the copper of which they consist had been separated when the mass was molten. On re-melting "blue metal" the whole of this separated copper disappears, and a perfectly homogeneous liquid is produced.[3]

I have now presented such information as I have been able to obtain respecting the mode of existence of copper in a molten mass of copper and lead. The phenomena accompanying the liquation of a solid mass of copper and lead may, it appears to me, be simply and perfectly explained by accepting the solution view, as I shall now endeavour to show. When the liquation cakes are heated in the first operation in the manner previously described, a certain quantity of the lead trickles out and the cakes diminish proportionately in volume; but the cakes after this treatment retain, say, about 25 per cent. of their weight of lead. Why so much lead should remain in the liquated cakes is intelligible from the considerations which were adduced in the early part of this article, and which need not here be repeated. And why the proportion of copper in the lead separated should be so constant, may also be easily explained, if we admit that molten lead acts as a solvent upon copper; for, as the temperature at which liquation takes place is pretty constant, so it is reasonable to infer that the quantity of copper dissolved by the lead should be equally constant.

With regard to the extraction of the silver from argentiferous copper by liquation with lead, all that is certainly known at present is the simple fact; but, as evidence has been adduced to show that more or less of the copper separates from the lead in a crystallized state, during the cooling of the molten mass of copper and lead, analogy would lead us to infer that these crystals would either be free from, or contain less silver than, the original copper, especially as they were surrounded with molten lead, which is a powerful solvent of silver. It is true that in the experiments in which beautiful and distinct crystals of copper were seen in the lumps of metal, the cooling

[3] This subject has been fully considered in the Author's volume containing the subject of Copper Smelting.

of the molten mixture of copper and lead had been very slowly effected. But if distinct crystals were produced in this case, crystals ought also to be formed in the opposite case; namely, that of rapid cooling, only they would be smaller and more confused. The size of the crystals might affect the proportion of silver separated from the copper; but the general fact remains, that, unless chemical affinity intervenes, one body tends to free itself from another by crystallization. A better example could hardly be quoted than that of the separation of silver from lead by the crystallization of the latter in Pattinson's process.

Analogy, however, is not always a safe guide. Thus, in the process of desilverizing lead by zinc, it is the latter which solidifies and extracts the silver from the liquid lead. Again, Schlüter found that gold was not separated in sensible quantity from auriferous copper by liquating the latter with lead; and if this be true, it may be inferred that, by liquating a mixture of auriferous lead and copper, the latter would in great measure extract the gold from the former. Whatever the true theory may be of the extraction of silver from argentiferous copper by liquation with lead, I repeat, all that can be certainly asserted at present is the fact of such extraction.

The quantity of lead left in the liquated cakes may be taken, on the average, at about 25 per cent. of their weight; and the object of the drying process is the extraction of as much of this lead as is economically practicable. That object is effected, as we have seen, by simply re-heating these cakes more strongly and for a longer period than in the first liquation. But the degree to which liquation can be carried in this second liquation must be determined by the conditions of temperature which have been previously considered (see p. 347): it should not be increased beyond the degree at which the cohesive force amongst the particles of copper ceases to be effective in causing contraction of the mass of copper. The drying process is, in fact, only a second liquation. The lead is extruded exactly in the same manner as in the first liquation; but, owing to the kind of furnace used in this process, it becomes oxidized as fast as it separates. Oxidation is in no way concerned in the actual liquation of the lead, and is only an accident of the process; and, doubtless, it would be possible to effect this second liquation equally well without the formation of any oxidized product at all, as, for example, in a retort from which atmospheric air is excluded, which was done in Nevill's process.

The phenomena observed in the drying process are also quite consistent with the solution view. As the temperature in this process is much higher than in the first liquation, the solvent action of molten lead on copper should be proportionately greater in the former than in the latter; and that is precisely what has been demonstrated by Karsten in his analyses of the oxidized product or "Darrost," recorded at p. 333 in a tabular form. In the first liquation the ratio between the copper and lead in the metal separated is, on the average, 2·5 : 97·5; whereas, in the second liquation or drying

rocess, it is 6·61 : 93·51, or about 3 times as great, the lowest xtremes in eight analyses being 4·40 and 91·03, and the highest 97 and 95·60. In the second stage of the process, in which the mperature was lowered, it will be seen on reference to the same ble that the quantity of copper which escaped along with the lead as relatively reduced; and in the third or last stage, in which the mperature was raised, it was relatively increased.

Even after this prolonged heating, a considerable quantity of lead till remains in the coppery residues, the average in five different ieces amounting to 14·1 per cent. of their weight. Although this uantity would probably have been reduced by prolonging the drying rocess, yet it might not have been profitable to do so; and in all etallurgical operations on the large scale the consideration of profit s of necessity paramount. But a limit there must be to the extrac- ion of the lead for the reasons assigned in an earlier part of this rticle. Moreover, the more coppery the lead becomes, the greater, robably, will be its adhesiveness; and if so, the greater resistance vill it offer to the cohesive force of attraction exerted by the copper. In the description of the drying process it is stated that persons xperienced in the practice of liquation differed in opinion as to whether the temperature should be gradually and continually raised during the process to the highest degree found practicable without causing the copper to melt, or whether it should be raised, lowered, and finally raised again. These are questions which only experience can conclusively decide; but the balance of opinion, if I err not, was in favour of the first course, and that course seems to me to be indicated by what has been stated in the considerations respecting the theory of the liquation process which I have now presented.

Karsten's Theory of the Process of Liquation.

Karsten, it will be recollected, adopts the conclusion of most of the old metallurgists with respect to the composition of the liquation cakes, and holds that, in order to obtain the best results, they should consist of 11 parts of lead and 3 parts of copper, by weight. Now these proportions are nearly in the ratio of 1 equivalent of lead to 1 of copper; and hence he infers that the metallic mixture forming the cakes is a definite chemical compound of the formula PbCu [idem]. In support of this inference he adduces various arguments. "So long," he says, "as it (*i.e.* the mixture, or as he terms it the "combination of copper and lead") is in a molten state, it must, on account of its perfect homogeneousness, be regarded as a perfect chemical combination of both metals. When it cools quickly, as is always the case in the receiving-pit of the mixing furnace, since water is poured upon it with a view to hasten its solidification, it remains homogeneous, and there is consequently no ground for maintaining that it is something else than a chemical combination of both metals."[4]

[4] Archiv, 1st series, 1825. 9. p. 22.

The assertion of Karsten, that the homogeneousness of a *molten* mixture of lead and copper is a proof of its being a definite chemical compound, is obviously so gratuitous and unfounded as not to need refutation; but the same could not be said of a *solid* homogeneous mixture of those metals, though even in this case the proof of chemical combination would be merely presumptive. This latter kind of proof is adduced by Karsten in support of his chemical combination theory: thus he states that when a molten mixture of 3 parts of copper and 10 parts of lead, by weight, is poured into an iron ingot-mould and quickly solidified, the ingot is perfectly homogeneous.[5]

On this subject I made the following experiment:—To 2683 grains of molten copper 9838 grains of molten lead were gradually poured (*i.e.* in the ratio of 3 : 11), and the mixture, after having been well stirred with a piece of wood, was rapidly poured into cold water. The granulated metal was in pieces varying much in size, some of it being in small shot-like grains, some in ragged bits such as are usually produced in the mode of granulation, and some in lumps. The metal was much harder than lead, yet it could be cut with a knife; it was comparatively tough, but frangible, though it required considerable force to break it. I examined the fracture of several pieces of it both with high and low powers under a compound microscope, as well as with an ordinary lens and the naked eye. The texture was finely granular and uniform in colour, which was lead-grey; I could not detect in any of the fractures the slightest appearance of copper-coloured grains: the metal, in fact, appeared to be homogeneous. I flattened one of the largest pieces with a hammer, filed one of the surfaces with a coarse single-cut file, and then rubbed it in various directions as well as circularly, first with pumice-stone, and finally with the fractured end of a piece of charcoal, with the addition of water. To my surprise, by such rubbing, it immediately acquired a copper-red tint. The experiment was repeated several times with charcoal alone, as well as with pounded marble *without* water, and with the same result. On scraping the reddened surface with a steel instrument, the original lead-grey colour was restored; but the copper tint instantly reappeared on again rubbing the scraped surface with charcoal and water. Very fine dark-coloured powder was copiously produced by this treatment, the mixture of which with water adhered tenaciously to the fingers. This red tint could not be due to a superficial tarnish, because it appeared *immediately* on rubbing. Now, if the metal had actually consisted of a chemical combination of lead and copper, as Karsten asserts, I am at a loss to account for the development of the copper-red colour under the conditions stated; whereas, if it were merely a most intimate mechanical mixture of the two metals, the development of that colour may, I think, be easily explained. Lead and copper differ very widely from each other in softness; so that on rubbing a mixture of those metals with a comparatively soft substance, such as charcoal,—no matter how intimate

[5] Archiv, antea cit. p. 27.

he mixture, so long as it is only mechanical,—lead should be removed n greater proportion than copper, and a copper-red tint should, t is conceivable, be produced. If this explanation be accepted, the acts above recorded conclusively refute the opinion of Karsten, hat a liquation cake, however homogeneous it may appear to the ye, is a definite chemical compound.

Karsten states that when such an apparently homogeneous ingot of lead and copper produced by rapid cooling, and consisting of the proportions of the two metals previously specified, is "carefully kept heated to redness, which is not sufficient to cause complete fusion, the effect of this heating is very different, according as the ingot is suddenly or slowly cooled. After sudden cooling by dipping in water, two wholly different metallic mixtures are seen on the fractured surfaces, which are very clearly to be distinguished by their red and grey colours respectively. By slow cooling in the air, the fractured surface of the ingot acquires the same homogeneous appearance as it had before heating to redness. Heating to redness also causes a separation, which is again removed by slow cooling. This separation, consequently, takes place before the mixture becomes fluid, and might even be prevented, if the mixture had become fluid, provided that, by a special arrangement, the more easily fusible compound, which separates in the fluid state, were not removed from the less fusible compound." [6]

I have not repeated the experiments of Karsten above described, nor do I consider it necessary to do so after what has been advanced. But I did re-heat to redness for a few moments a piece of the apparently homogeneous granulated metal previously referred to; and found that afterwards its fractured surface showed distinctly a mixture of copper-red and lead-grey particles.

Considering the mixture of which the liquation cakes are formed as a definite chemical compound, Karsten, as previously stated, maintains that by liquation this compound is resolved into two other definite compounds: one—the cupriferous lead separated—having the formula $Pb^{12}Cu$ [idem]; and the other—the residual plumbiferous copper—having the formula $Cu^{12}Pb$ [idem] (see p. 324). But this conclusion is merely an opinion, which rests entirely on the fact that the composition of those two substances may be approximately indicated by the above formulæ. I have, however, endeavoured to show, that on the solution theory (see p. 351), the composition of those substances might be expected to be pretty constant, because the proportion of copper dissolved by molten lead depends upon temperature, and must, therefore, be constant at any given temperature; and that the temperature to which the liquation cakes are exposed is subject only to comparatively slight variation, no doubt can be entertained. The same reasoning applies also with equal force to the products of the drying process; but as in this process there is greater variation in temperature than in the first operation of liquation, the

[6] Archiv, antea cit. p. 28.

ratio between the lead and copper in the oxidized product (*Darrost*) is not so constant as in the latter, the proportion of copper, according to Karsten's own experiments, increasing as the temperature increases. Comparative constancy, therefore, in the composition of the products separated in the two operations, may be regarded as the accident of temperature, and not as necessarily indicating the formation of two definite chemical compounds of lead and copper, as Karsten maintains.

It may be thought that I have devoted too much space to the consideration of this nearly obsolete process of liquation; but I have done so because it is important, in my opinion, that modern metallurgists should be thoroughly acquainted with the processes of the past, not alone on account of their historic interest, but also because much may be learned from the careful study of such processes. We have seen how many questions of real value in a physical as well as chemical point of view may arise from the consideration of the process of liquation, and questions, moreover, the solutions of which may possibly throw light on some of the phenomena of metallurgical operations still in use.

SEPARATION OF GOLD FROM SILVER BY SULPHUR.

Sulphur when heated with gold has no action upon it; but the reverse is the case with silver, sulphur attacking it energetically and forming sulphide of silver. Hence, by heating an alloy of these two metals with sulphur, at first gently and then to the melting-point of gold, the silver is separated in the state of sulphide and the gold in the metallic state. But if the gold be present in comparatively small proportion, there would be a risk of losing much of it, if a considerable quantity of silver were not left unchanged, with which it might alloy. Moreover, as the gold, which is separated by sulphur from silver, must be very finely divided, it remains in a certain degree suspended in, and diffused through, the molten sulphide of silver. From this mass, while molten, it may be abstracted by the intermixture of metallic silver, which lays hold of the finely-divided gold, alloys with it, and subsides in one mass to the bottom of the vessel in which the operation is conducted; and this is what is done in the process presently to be described in the operation termed precipitation.

But, although sulphide of gold cannot be formed by heating gold with sulphur, and although sulphide of gold is immediately and completely reduced when heated *per se*, the whole of the sulphur being volatilized, yet it is by no means certain that, when in contact with a mass of other sulphides (excluding such as the alkaline sulphides, which *do* convert gold into sulphide with the aid of heat), some sulphide of gold may not be formed by the action of sulphur, and that, under the condition stated, sulphide of gold may not be capable of resisting the decomposing action of heat. Analogy would lead us to infer that this might be the case. Thus, I roasted an

auriferous silver ore, containing blende in large quantity, galena, iron-pyrites, and a small quantity of copper-pyrites, and in the latter part of the process raised the temperature to bright-redness, yet out of that roasted ore a sensible quantity of gold was dissolved by a solution of hyposulphite of soda. But I found that this solution did not appear to exert the least action on gold-leaf; whence I inferred that the gold extracted by the hyposulphite solution from the ore existed therein in the state of oxide, by reason of its association with other oxides in large quantity;[7] for oxide of gold could certainly not have existed *per se* at the temperature to which the roasted ore had been raised. Analogy, however, may lead to erroneous inferences, and the question here raised can only be solved by experiment. These introductory remarks apply equally to other processes to be subsequently described, in which sulphur, either free or combined, is the agent for the separation of silver.[8]

The earliest account which I have met with of the use of sulphur for separating gold from silver is the following by Theophilus, *alias* Rugerus, the artist-monk, who wrote in the first half of the eleventh century.[9]

"When you have scraped the gold from silver, place this scraping in a small vessel, in which gold or silver is accustomed to be melted, and press a small linen cloth upon it that nothing may be ejected from it by the blast of the bellows, and, placing it before the furnace, melt it; and directly lay fragments of sulphur in it, according to the quantity of the scraping, and carefully stir it with a thin piece of charcoal, until its fumes cease; and immediately pour it into an iron mould. Then gently beat it upon the anvil, lest by chance some of that black may fly from it which the sulphur has burnt, because it is itself silver. For the sulphur consumes nothing of the gold, but the silver only, which it thus separates from the gold, and which you will carefully keep. Again melt this gold in the same vessel as before, and add sulphur. This being stirred and poured out, break what has become black and keep it, and do this until the gold appear pure. Then place together all that black, which you have carefully preserved, upon a test made of bone and ashes, and add lead, and so burn it that you may recover the silver." [I have given Hendrie's translation nearly *verbatim*, having only altered a word or two to make the meaning plainer.—J. P.]

The following account of the process is by Schlüter, and the object was only a partial separation of silver from an alloy of gold and silver, containing so small a proportion of gold that it could not, with profit, be directly parted by nitric acid. Refined auriferous silver is most suitable for this treatment, though it is

[7] Philosophical Magazine, 1850. 36. p. 2.

[8] Gründlicher Unterricht von Hütte-Werken, 1738. Probier-Buch, forming the second part of the treatise, pp. 171–175.

[9] An Essay upon Various Arts in three Books, by Theophilus, called also Rugerus, Priest and Monk. Translated, with notes, by Robert Hendrie. 1847. pp. 316–319.

also applicable to partially-refined silver, the "blicksilber" of the Germans, and to silver alloys; and the silver should not contain more than 1 dram, nor less than $\frac{3}{4}$ grain of gold, per mark. The silver is granulated, and, while wet, mixed with $\frac{1}{8}$ of its weight of pounded and sifted sulphur, which adheres to the wet metal; but for each mark (8 ozs.) of silver mixed with sulphur, $1\frac{1}{2}$ oz. of silver is reserved unmixed with sulphur. The mixture is heated in a covered crucible, and at first the temperature is kept below the melting-point of silver, in order that the sulphur may remain largely in contact with the silver, and combination, or, as Schlüter terms it, cementation, be thereby effected; but, afterwards, the temperature is raised until the contents of the crucible are melted. An hour after fusion, one-third of the reserved granulated silver is thrown into the crucible, and, when the whole is melted, the molten mass is stirred with a stick, and not with an iron rod, because in that case sulphide of iron is formed and combines with the sulphide of silver, causing much inconvenience in the after-treatment. Stirring should be repeated after the lapse of half an hour. Another third of the reserved silver is added an hour afterwards, and the last third an hour later when the precipitation is finished. The mass, after the last addition of silver, is kept molten for at least three hours, stirring being repeated every half-hour, unless the following appearances occur previously. When the "plachmal" becomes white at the top, and drops of pure silver, about as large as peas, are perceived, the crucible may be taken out of the furnace and the contents either laded or poured into a metal ingot-mould previously heated and greased; and for this purpose a mould, with a rounded bottom like a mortar, is recommended by Schlüter as preferable to a conical one, pointed at the bottom. Or, if the quantity be not large, it is better to let the mass cool in the crucible, and break the latter afterwards; and this plan is superior to pouring out; because the lump of metal is much better formed, more level at the top, and separates better from the "plachmal," to which it adheres so strongly that a hammer is required to detach it. As the line of junction between the lump and the "plachmal" may be easily seen, a chisel is applied in that direction, and struck with a hammer until the "plachmal" flies off; but if this should fail, the mass may be heated in a crucible until the "plachmal" is melted when the lump of metal, which is less fusible than it, is taken out in this way the whole of the metal is sure to be collected in the lump, whereas, when the chisel is used, some of the metal may remain attached to the "plachmal."

It is sufficient if the gold from 100 marks of silver be concentrated in a lump of 8 or 10 marks; but if the original silver were very rich, the lump might be larger. Should all the gold not have been thus collected, and assays of the "plachmal" show that it retains gold, the latter should be re-melted with the addition of $\frac{1}{2}$ oz. of reserved granulated silver per mark, and kept molten for $1\frac{1}{2}$ hour longer; but, failing a supply of such silver, a little iron may be sup-

ituted for it, in which case the "plachmal" need not be kept molten or more than half an hour afterwards. If the metal produced by melting together the lump from this fusion and that previously obtained be found to be too rich in silver to admit of being profitably parted by nitric acid, it would be necessary to granulate it and subject it to the same treatment with sulphur as that above described. The metal, in which the gold has been concentrated, is granulated and cupelled with the addition of lead, on a test of wood-ashes, and the resulting auriferous silver is parted by nitric acid.

The silver is recovered from the "plachmal" by the following method. If the precipitation of the gold has been effected only by silver, without iron, so that the "plachmal" is wholly composed of sulphur and silver, it is cupelled on a test composed of 2 parts of pounded bricks and 1 part of pounded glass, well mixed together, moistened, and rammed in a bowl-shaped vessel of iron, a little bone-ash being afterwards sifted over the cavity.[1] If wood-ashes were used, the sulphide of silver would penetrate them even to the iron, and form a sort of paste with them. During the cupellation of "plachmal" of which the precipitation has been completed with the addition of a little iron, or when the contents of the crucible have been stirred with an iron rod, as soon as the sulphur has been evolved the iron appears spread over the silver like coarse sand, and must be skimmed off.

This process was in use at the Mint at St. Petersburg in the last century; and it is stated that in 1797 the actual loss of metal (*i.e.* of silver and gold) amounted only to 0·16 per cent., whereas, previously, it had amounted to 2·1 per cent.[2]

Summary of the process.—It consists of the following operations:—

I. Granulation of the auriferous silver.
II. Partial sulphurization of the granulated metal by heating it with sulphur.
III. Precipitation of gold from the sulphide of silver by some of the granulated auriferous silver reserved for that purpose.
IV. Cupellation of the enriched (*i.e.* with gold) lump of silver with the addition of lead, and parting of the product by nitric acid.
V. Cupellation of the sulphide of silver.

It may be asked, why the enriched lump of silver should be cupelled with the addition of lead before parting with nitric acid? Although no reason for this course is assigned by Schlüter, yet there was, doubtless, a good one; probably the presence of sulphide of silver in notable quantity in the lump, which would occasion some inconvenience in the operation of parting. (See pp. 25 and 26 antea.)

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[1] For further information on this subject, see the Author's volume on the Metallurgy of Lead, p. 210.

[2] Crell's Chemische Annalen, 1797. Part I. p. 115.

SEPARATION OF GOLD FROM SILVER BY SULPHUR AND IRON.

This process is similar in principle to that last described, and i conducted in the same manner; and the only substantial differenc between them is, that in the one silver is used and in the other iro for the precipitation of the gold. Indeed, in the account of the forme it is stated that, when sufficient granulated auriferous silver ha not been reserved, a little iron is added as a substitute for silver. A long and very detailed account of this process is given by Schlüter, from which it is only necessary to extract a few particulars. An ounce of sulphur is used per mark of silver, whether imperfectly refined or completely so; but for alloyed silver 1 oz. 2 drams is the proportion. "Plachmal" from the first fusion is cast in a conical shape, and when solid is put back into the crucible, with the point uppermost, where the lump of metal would be; and if such a lump be observed, it is withdrawn after the fusion of the "plachmal" and put aside. If there be no lump, it matters not, for the cementation has not therefore failed: this result indicates that the particles o granulated metal were too small. But if, on the contrary, there b a large lump, the particles were too large and not sufficiently hollow This inconvenience may be avoided by sifting the grains befor mixing with sulphur, and granulating them again. A lump o 5 marks from 100 marks of silver is good work. In the second fusio $1\frac{1}{2}$ lb. of iron is added; and in the case of alloyed silver $1\frac{3}{4}$ lb But if, in the cementation stage, there be no lump, the iron must b increased by $\frac{1}{2}$ lb., and decreased by $\frac{1}{2}$ lb. or 12 ozs. if the lump be to large. In the third fusion $\frac{1}{2}$ lb. more iron is added. The "plachmal is assayed for gold after this fusion, and if found to be free from gol which is very rarely the case, and if the lumps from 100 marks o the original silver do not exceed 12 or 15 marks in weight, th "plachmal" is ready for further treatment. But if it still contai gold, it must be re-melted and another $\frac{1}{2}$ lb. of iron added; and the lumps be too large, they must be granulated, cemented wit 6 drams or 1 oz. of sulphur per mark, and so forth. The size of th lumps should be determined by the proportion of gold which the contain: in those produced in this process from the richest auriferou silver, $\frac{1}{2}$ oz. or at most 1 oz. of gold per mark is quite sufficien The lumps are cupelled on a test, and the resulting auriferous silv is granulated and parted by nitric acid.

The silver is thrown down from the molten "plachmal" by iro of which usually a total of 9 lbs. is required for the quanti produced from 100 marks of original silver; at first 6 lbs. a added, and the remainder at intervals, until in fact the iron ceas to be acted upon. After this, 2 lbs. of litharge are added, in orde it is stated, to facilitate the separation of the metal from the regul of sulphide of iron. The metal is cupelled on a test.

As the regulus from the last operation still contains much silv it is pounded, mixed with half its weight of litharge, and th melted in a crucible. The lead thus separated is cupelled along wi

other silver. But as the regulus, after this treatment, contains a little silver, it is put aside to be smelted with the refuse of furnaces.

Summary of the process.—It consists of the following operations:—

I. Granulation of the auriferous silver.
II. Partial sulphurization of the granulated metal by heating it with sulphur.
III. Precipitation of gold, along with some of the silver, from the sulphurized metal produced in No. II.
IV. Cupellation of the metal from No. III., and parting of the product with nitric acid.
V. Precipitation of the silver from the sulphide of silver, after treatment in No. III., by metallic iron and litharge, and cupellation of the precipitated silver.
VI. Melting of the sulphide of iron and silver, after treatment in No. V., with litharge, and cupellation of the resulting argentiferous lead.

SEPARATION OF GOLD FROM SILVER BY SULPHUR AND LITHARGE.

This process was formerly practised at Oker (or Ocker as it is sometimes spelt), near Goslar, Lower Harz, in the then kingdom of Hanover. The silver produced from the ores of the Rammelsberg mines is auriferous; and it is this silver which was the subject of the treatment about to be described, for the purpose, not of separating completely the gold and silver from each other, but of concentrating the gold in a small portion of the silver, so as to obtain an alloy that might be profitably parted by nitric acid. The latest and most detailed description of this process which I have met with was published in 1836 by Dr. J. L. Jordan, of Clausthal;[3] and, as I hold that no description of a metallurgical process is of much practical value unless it be detailed, I shall present a really literal, though somewhat abridged, translation of Jordan's paper. In 1805, Lampadius published an account of this method of parting by sulphur and litharge at the Oker works; and he states in 1839, that, having read Jordan's paper, he found it to contain nothing which he had not previously described;[4] which is satisfactory, as showing that we have two accounts by different observers which agree, though one was written 24 years after the other. A condensed and lucid description of the process is given by Lampadius in his "Elements of General Metallurgy,"[5] and in some respects I think it is better than that of Jordan.

The "blicksilber" contained on the average 14 loths 17·5 grains of fine silver per mark (or 93·6 per cent. of fine silver), and 0·75 grain

[3] Journal für praktische Chemie, 1836. 9. pp. 74–84.

[4] Die neuern Fortschritte im Gebiete der gesammten Hüttenkunde, etc.; Freiberg, 1839. p. 132. The description here referred to appeared in his "Handbuch der allgemeinen Hüttenkunde," 2. p. 144.

[5] Grundriss einer allgemeinen Hüttenkunde; Göttingen, 1827. p. 269.

of gold (= 0·26 per cent., or 84 ozs. 18 dwt. per ton of silver). According to Lampadius, the silver contained from 0·75 to 4 grains of gold per mark.[6] For information concerning "blicksilber," the reader is referred to the Author's volume on the Metallurgy of Lead: it is silver which has been only partially refined in the ordinary German furnace, named the "Treibofen," and contains lead, copper, possibly also antimony, arsenic, cobalt and nickel in small proportions.

According to Lampadius, "blicksilber" is from 14 to 15 loths fine (*i.e.* the mark of 16 loths contains from 14 to 15 loths of fine silver), and varies very much with respect to the nature of the impurities with which it is associated, and which are lead, copper, nickel, cobalt, and occasionally traces of arsenic. "Blicksilber" from the Halsbrücke smelting works at Freiberg was proved by Lampadius to have the following composition per cent.:[7]—

"BLICKSILBER."

Silver	92·180
Lead	4·210
Copper	2·104
Nickel	0·600
	99·094

Granulation of the "blicksilber."—The process commences with the granulation of 600 marks of "blicksilber," the cakes of which are broken into pieces of suitable size for melting in crucibles; and as silver becomes easily frangible at a red-heat, the cakes are made red-hot and then broken. A crucible being set in a melting furnace, the pieces of silver are dropped into it, covered with powdered charcoal, and heated to such a degree as to render the metal very liquid, the crucible having been previously closed with an iron cover. The metal is laded out, either with an iron ladle coated with loam, or a small plumbago crucible, and poured in a thin stream into a copper vessel immersed in cold water. During the pouring, the water under the stream is rapidly stirred with a stick or besom, in order to prevent the grains from adhering to each other. When the granulation has been properly conducted, the grains are small, roundish, thin, and foliated.

Sulphurization of the "blicksilber."—This operation is effected in a crucible, which should not be contracted towards the top, but wide upwards, in order that after the operation is completed, and the contents have become cold, they may be removed by inverting the crucible, without injuring it, so as to make it unfit for further use. The granulated metal, while still wet, is mixed with $\frac{1}{8}$ of its weight of powdered sulphur, much of which adheres to it, and the mixture is put, in successive portions, into a plumbago crucible previously

[6] Grundriss, antea cit., p. 269.
[7] Handbuch der metallurgischen Hüttenkunde. Kerl, 1861. 1. p. 733.

set in the furnace; and it is best to have most of the sulphur towards the bottom. The temperature is carefully and gradually raised, when the moisture evaporates and the silver and sulphur afterwards combine. The mixture, while it is settling down in the crucible, should not be too liquid, as, in that case, some of it not yet dry might come in contact with metallic sulphide already formed underneath and cause explosions, attended with the projection of silver out of the crucible. When the temperature is too high, the molten sulphur rises above the metal and is wastefully volatilized. As soon as the portion of the mixture first put into the crucible has sunk a little, a second portion is added, and so on until the crucible is full. The thorough sulphurization of the granulated silver is, it is hardly necessary to remark, an important part of the process.

With reference to the sulphurization, Lampadius states that the wet granulated silver is mixed with 2 loths of sulphur powder per mark, and introduced in successive portions into a crucible heated to moderate redness, and at first is strongly sintered together (or, as we generally term it, fritted), or *cemented*. Schlüter also, in describing the sulphurization of silver by sulphur in another process, lays stress on the importance of such *cementation* in the early stage of this operation. The sulphur is by this means kept largely in contact with the silver; and though the temperature be comparatively low, yet it is high enough to cause the sulphur to act energetically on the silver. The case is analogous to the fritting of a mixture of silica and oxide of lead, as described in the Author's volume on the Metallurgy of Lead.

Precipitation of the gold.—As the gold, which has been separated from the silver by the sulphur, is diffused in a finely-divided state through the mass of sulphide of silver, it is extracted therefrom by means of lead. For this purpose litharge is now added in small quantities at a time, when metallic lead is immediately set free (see p. 38 of this volume), and decomposes an equivalent proportion of the sulphide of silver in the regulus, with the formation of sulphide of lead and sulphurous acid, and the liberation of metallic silver. This silver unites with the finely-divided gold and gradually subsides to the bottom of the crucible, forming what is termed enriched metallic bottoms.[8] But a small quantity of lead alloys with the silver which it has set free, passes into the bottoms, and protects them from the action of the sulphur of any sulphide in the regulus, which may be decomposable by lead; and it is evident that the bottoms will become richer and richer in lead, the oftener this operation is repeated. But why, it may be asked, should litharge be added, because it seems, at first sight, to be undoing the

[8] "Metallkönig," literally translated, "metal-king." But as the term "bottoms" is used in our copper-works to designate a fused mass of metallic copper separated from copper-regulus in the process of making "best-selected copper," I have ventured to apply the same term to the lump of metal separated in the manner described.

work previously effected by the sulphur—namely, the sulphurization and consequent separation of the silver—and why should not some of the granulated silver be added instead of lead? The answer, I presume, is that in that state the contact between the silver and the finely-divided gold, diffused through the regulus, would be exceedingly limited, as compared with what it is when silver is separated from the regulus by the action of litharge; and, therefore, the gold would not be so well collected and carried down by the silver if granulated silver were substituted for litharge. But, as previously shown, the gold may be precipitated solely by granulated silver.

The proportion of litharge required is from about 1 to 1½ loth per mark of "blicksilber;" and the time occupied in the treatment with litharge is from 4 to 5 hours, a small quantity of it being sprinkled over the molten regulus every quarter of an hour. The regulation of the temperature in this stage of the process is most important: if too low, the molten regulus is not sufficiently liquid, and the settling down of the desulphurized metal is impeded, so that particles of gold, suspended in the regulus, are not sufficiently collected and precipitated: too high a temperature, on the contrary, makes the regulus too liquid, so that the silver separated by the litharge subsides too quickly to the bottom of the crucible, without laying hold of the gold in the degree desired. The temperature of the molten regulus is right, when its surface appears bright and without any decided movement, such as occurs so notably in cupellation, and when the litharge sprinkled upon it does not too quickly disappear, but is taken up by the molten regulus with a feeble hissing sound. The temperature is too low, when the surface of the molten regulus appears dull and without any such movement as that just mentioned, and when the litharge sprinkled over it remains a considerable time.

The litharge is generally strewn near the sides of the crucible because the particles of gold are always abstracted and deposited with more difficulty from the circumference of the molten regulus than from its central portion. After the whole of the litharge has been added, and the molten regulus has become sufficiently thin the firing is stopped, but the crucible is left slowly to cool undisturbed in the furnace. When cold, the mass is detached from the crucible by inverting the latter, as previously stated; and the enriched lump of bottoms is knocked off from the overlying regulus consisting of sulphide of silver and lead, with, it may be, the sulphides of other metals, such as copper, existing in the original "blicksilber;" this regulus is now termed "plachmal." The "plachmal" will be found coated over on the outsides (*Aussenseite*, by which, I presume, is meant the outer surface) with hair-like filaments of metallic silver, which are formed when, during the cooling of the "plachmal," atmospheric oxygen gets access to its upper surface, and also to its sides by the contraction which it suffers. (See p. 27 of this volume.)

The treatment of the "plachmal" with sulphur and litharge has

to be repeated four or five times in the manner above described; because one operation of the kind is not enough to free it sufficiently from gold. The hair-like silver having been first scraped off, the "plachmal" is placed at the bottom of the crucible; but, if broken in pieces, those which had been in contact with the enriched bottoms, as also those which had been coated with hair-like silver, are placed underneath the other pieces, or, at least, towards the middle of the crucible; because the former are still particularly rich in gold. The precipitation is then proceeded with as in the first instance. After the "plachmal" has been several times successively melted down, there appears upon its surface a crust, which, if not taken off, would impede further precipitation. This crust consists of fine particles of the substance of the crucible, of impurities which the "plachmal" occasionally acquires in the act of breaking it in pieces, of sulphate of lead resulting from the oxidation of the sulphide of lead in the "plachmal," of peroxide of iron, and of adherent particles of "plachmal." Should the operator wish to ascertain whether the gold has been well separated, a sample of the "plachmal" must be prepared for assaying from pieces taken from four different portions of its mass, which from the shape of the crucible is conical; namely, the middle, about 3 inches from the sides, the exterior of the sides, and, lastly, about 3 inches above the level corresponding to the upper surface of the bottoms in the last operation. The assay-sample is cupelled with the addition of three times its weight of lead, and the resulting button of silver is parted by nitric acid. But this, according to Jordan, is not a good way; because, during the action, dust-like particles of silver are projected and lost. A better method is to melt the assay-sample with three times its weight of potash, to cupel the resulting button of metal, and afterwards part by nitric acid. Usually, after the treatment of the "plachmal" by precipitation, 600 marks of "blicksilber" yield 150 marks of bottoms, which, however, are not yet rich enough in gold, and have to be granulated and subjected to further treatment with sulphur in the manner previously stated; and should fresh "blicksilber" be available, it may be used instead of litharge in the first precipitation. When all the "blicksilber" has been thus worked up, the bottoms are treated by themselves, frequently 10 or 12 times successively, litharge being used as the agent of precipitation. By this repeated treatment the bottoms become so leady that they must be cupelled in a muffle, so as to make them fine or nearly so, because, when there is much sulphide of lead in the "plachmal," the extraction of the gold is very imperfect. During this cupellation, the sulphurized particles of metal are so violently acted upon that, with the most careful firing, the muffle is often strewn over with metal in the finest grains, owing to the vigorous evolution of sulphurous acid gas. These grains are collected and parted, along with the metal left on the cupel. The gold is finally separated from the silver, in which it has been concentrated, by nitric acid: this operation, as practised on the large scale, will be described in a subsequent part of this volume.

Desilverization of the "plachmal."—The "plachmal" is broken into pieces 2 to 3 inches in diameter, and melted in a plumbago crucible, with the addition of ¼ of its weight of wrought-iron scrap. Part of the iron is laid on the bottom of the crucible, and the remainder, intermixed with the "plachmal," on the top. The crucible is heated in an ordinary melting furnace, at as high a temperature as the furnace will produce, and the contents are stirred several times with an iron rod. When iron can no longer be felt in the molten mass, desulphurization is completed, the fire is allowed to go down, and the crucible left to cool in the furnace. After cooling, the crucible is withdrawn and inverted, when the mass within it drops out; it consists of a lump of leady metal at the bottom, and of a layer of overlying poor regulus, which is knocked off with a hammer. The charge for a crucible is from 100 to 120 marks of "plachmal," from which a lump, containing from 60 to 80 marks of silver, is produced, which is cupelled fine in a muffle.

Treatment of the desilverized "plachmal" or residual regulus.—This regulus is roasted in a reverberatory furnace, and afterwards melted in a plumbago crucible, with the addition of 20 per cent. of its weight of iron; and when the whole is melted, 30 per cent. of litharge is added in small portions successively. The litharge is reduced, together with a little copper, by the action of the sulphur of the sulphides, and by the iron; and the separated metal is cupelled fine on a reverberatory test-furnace. The regulus resulting from the above reaction is melted along with the scrapings of the tools and crucibles used during the whole process, and the slags which are skimmed off in the precipitation of the "plachmals," the melting being effected in a plumbago crucible, with the addition of some iron and litharge: this operation is termed "Krätzschmelzen." A lead-lump of metal is thus obtained, which is cupelled along with the bottoms formed in the desilverization of the "plachmal," and in the first stage of the treatment of the regulus from that desilverization, as they still retain a little gold; but the lump should be previously assayed for gold. Lastly, the grains of silver got by washing the air-furnace ashes and pounded old crucibles, and so forth, are passed together through a low blast-furnace (*Krummofen*), in what is termed "Krätzfrischen," from which there are obtained three products; namely, argentiferous lead, regulus, and slag. The first product is cupelled, and the resulting silver worked up in the next batch of auriferous silver treated by the process under consideration; the second product, or regulus, is roasted three times and put aside for "Krätzfrischen;" and the third product, or slag, is thrown away.

Summary of the process.—It consists of the following operations:—

I. Granulation of auriferous silver.

II. Partial sulphurization of the granulated silver by heating it with sulphur: the products are enriched silver, and regulus of sulphide of silver, containing gold.

III. Precipitation of gold from the regulus in No. II. by

litharge: the products are auriferous silver containing lead, and a regulus of sulphide of silver and lead, containing gold.

IV. Desilverization of the regulus from No. III. by metallic iron: the products are silver, containing lead, and a poor regulus of sulphide of iron, containing lead and silver.

V. Roasting of the regulus from No. IV., and melting it with metallic iron and litharge: the products are argentiferous lead, with a little copper; and a regulus of sulphide of iron, but not free from lead and silver.

VI. Melting of the regulus from No. V., in conjunction with various argentiferous substances: the products are argentiferous lead, containing gold; and a regulus of sulphide of iron.

VII. Smelting in a low blast-furnace a mixture of various waste substances, containing lead and silver: the products are argentiferous lead; a regulus of sulphide of iron, not free from lead and silver; and a slag, which is thrown away.

VIII. Roasting of the regulus from No. VII. and melting it in operation No. VII.

IX. Cupelling the enriched silver, and parting by nitric acid.

SEPARATION OF SILVER FROM GOLD BY SULPHIDE OF ANTIMONY.

The object of this process is the complete separation of silver from gold which contains only a small quantity of silver.

It is sulphur that is really the agent by which silver is separated from gold in this process; but, as it is in combination with antimony, it may be kept in contact with the alloy of those metals at a much higher temperature than is practically possible when it is uncombined, the presence of antimony not interfering, because it has less affinity than silver for sulphur. Hence, on heating sulphide of antimony with such an alloy, sulphide of silver is formed and metallic antimony separated, which alloys with the gold. But in practice it is found necessary to use a much larger proportion of sulphide of antimony than theoretically ought to suffice to sulphurize the silver. The process of separation by this method comprises three operations; namely, the sulphurization of the silver, the separation of the antimony from the alloy of gold and antimony, and the recovery of the silver from the regulus, consisting of sulphides of silver and antimony. Sulphide of antimony also sulphurizes copper or any other metal with which the gold may be associated, and which, with the aid of heat, decomposes that sulphide; but, obviously, separation of the gold could not be properly effected if the sulphide or sulphides formed were not fusible at the melting-point of gold. Platinum, it may be here stated, is not acted upon by sulphur, and therefore remains with the gold. The great eulogist of antimony, Basil Valentine, who lived in the 15th century, thus wrote with regard to its purifying

power:—"Sciant ergo homines antimonium non tantum aurum purgare, mundare, et ab omni peregrina materia, omnibusque aliis metallis liberare, sed enim efficere vi sibi innata in hominibus, et pecudibus."[9] The old chemists termed antimony "Balneum Regis" or "Balneum Solis," and "Lupus Metallorum," from the purifying effect which its sulphide exerts upon gold.[1] Schlüter, also, at a much later date, the 17th century, expresses the opinion that gold could be made finer by means of sulphide of antimony than even by parting with nitric acid.

The process is certainly of very ancient date, and was formerly much used, and continued to be practised down to a comparatively recent period; but now, I believe, it is obsolete, unless perhaps with some conservative goldsmith, or in some outlandish locality or other. It was a great favourite of the old metallurgists, and copious descriptions of it occur in the treatises of Biringuccio, Agricola, Ercker, and others. In my opinion, however, the best account of it was published by Schlüter in 1738, of which I find that Lewis appears largely to have availed himself in his article on Gold in his treatise entitled "Commercium Philosophico-Technicum," published in 1763. There is also a good description of it in Macquer's Chemical Dictionary, of which an English translation appeared in 1771. I have followed the example of Lewis, and drawn largely on Schlüter in the description which I now present.[2]

Only good sulphide of antimony should be used: the more striæ or needles there are in it, the better it is; and if the needles are not well arranged, it should be rejected: that which is at the surface of the cakes (which are obtained by the liquation of the native sulphide) should not be used in this process.

Biringuccio, in his description of the process, states that either sulphur in the form of sticks or rolls, or sulphide of antimony, may be used, or both together.

Good crucibles are essential in the sulphurization part of the process, and Schlüter recommends those of Passau and Ipsen, but not those of Hessen; though, as will be seen hereafter, Hessian crucibles were used at a comparatively recent period in this part of the process at the Dresden Mint.. The crucible should stand in the furnace on a large flat scorifier, so that if during fusion any of the contents should rise and run over the sides, as too often happens, the gold carried away at the same time may be collected.

According to Lewis, "one of the greatest difficulties in this process regards the crucibles, which are very liable to crack, and to be corroded by the sulphureous matter. Scheffer relates that the

[9] Theodori Kerckringii Doctoris Medici Commentarius in Currum Triumphalem Antimonii Basilii Valentini. Amstelædami, clɔ Iɔc Lxxxv. p. 187. "Let all men therefore know that antimony not only purges, cleanses, and frees gold from all foreign matter, but also, by its innate force, men and cattle."

[1] Gold was named the "King" or the "Sun," and the meaning is, that by taking a bath of antimony the monarch was washed or purified; and that the "Wolf of the Metals" devoured all other metals with which the monarch might be associated.

[2] Op. antea cit. pp. 178–188.

ucibles he has found to be most durable are those which had been eeped several days in linseed oil; then cleared from the oil, so as remain only of such a degree of moistness, that some borax in ne powder may adhere and be spread all over the inner surface; and fterwards set by to dry slowly: in a crucible thus prepared, he says, e can perform two or three hundred fusions." [8]

The furnace described by Schlüter is a simple chamber, without ny grate at the bottom, and is supplied with a blast of air from orge-bellows, charcoal being the fuel.

The proportion of sulphide of antimony should be regulated by hat of the silver or other metal in the alloy. Gold, says Schlüter, which has been parted with nitric acid, requires only twice its weight of the sulphide, but 3 or 4 times as much when it contains a considerable quantity of silver or copper. In Macquer's account it is recommended to add sulphur along with the sulphide of antimony, in order to obtain an alloy of gold and antimony, containing less of the latter metal than would be the case if sulphide of antimony alone were used; and so to save time and trouble afterwards in separating the two metals from each other, the expulsion of the antimony being a very tedious operation. Lewis also, for the first of these reasons, directs that the sulphide of antimony should be mixed with $\frac{1}{4}$ of its weight of sulphur.

According to Agricola, the proportions by weight of argentiferous gold and sulphide of antimony should be 1 : 3; and if the gold be free from copper, it should be first melted with 1 loth of that metal per mark of sulphide of antimony, but with only $\frac{1}{2}$ loth if it already contain copper. The reason assigned by Biringuccio for this addition of copper is that it "occasions the better heating of the bath and makes it more liquid (*più suttile*)."

Much of the gold should not be put into the crucible at a time; or the risk of loss of gold is great enough when only 3 or 4 marks are operated upon. When the contents of the crucible are perfectly melted, a third of its capacity should remain void, because, as before intimated, "the antimony rises easily;" that is, as Lewis writes, "swells and froths up." As soon as the gold is melted the sulphide of antimony is added, according to Lewis and Macquer, in the state of powder; and when the molten mass begins to emit sparks, it is poured immediately into a conical ingot-mould of iron or brass, wide at the top, and previously smeared over with grease (or, Agricola and Perez de Vargas say, wax) or blackened with the smoke of an oil-lamp, and then heated to such a degree as scarcely to be held in the hands. Lewis directs that the mould should be gently struck or jogged so as to produce a tremulous motion of the fluid matter, by which the settling of the gold is promoted. The mould should be large enough to hold the whole contents of one crucible. When solidification has

[8] Commercium Philosophico-Technicum. By W. Lewis, M.B. and F.R.S. London, 1763. p. 156.

taken place, the mould is inverted over an iron table, and, if necessary, tapped, when the gold usually separates from the mass as it drops out; but if not, it may be easily detached from the regulus by a few blows with a hammer. As soon as the crucible is emptied, it is replaced in the furnace and covered, in order to prevent it from cracking by contact with the cold air. The gold is put back into the crucible and melted with the addition of twice its weight of fresh sulphide of antimony, and this operation is again twice repeated, each time with the addition of twice as much sulphide of antimony as the lump of antimonial gold weighs after each fusion; and when it is desired to make the gold extremely fine, the lump, after the third fusion, is re-melted with twice its weight of fresh sulphide of antimony. The regulus from this fusion being still slightly auriferous, is afterwards desilverized along with the regulus from each of the preceding fusions. During these fusions great care should be taken to keep the crucible well covered, lest charcoal might fall into it, in which case the molten contents would rise and overflow. In these last fusions the gold does not receive much addition from the antimony, as the reduction of that metal from its sulphide is only proportionate to the sulphur absorbed by the metal or metals alloyed with the gold; and in the fusions the greater part of such metal or metals has been sulphurized and removed.[4]

The alloy of gold and antimony is melted in a good Hessian crucible, and not in one of Ipsen, because it is alleged that gold of a more beautiful colour is obtained with the former.[5] The crucible should be well covered to prevent any charcoal from falling into it. When the alloy is melted, the forge-bellows are stopped, and air is blown upon the metal with a hand double-bellows (*i.e.* a double-bellows, which may be held in the hands), to the nozzle of which is fixed a copper tube bent nearly at a right angle at the free end; so that the blast may be injected downwards into the crucible, while the bellows are held horizontally. Copious fumes of oxide of antimony are evolved, and the blowing is continued until the greater part of the antimony has been expelled; the signs of which are, the gold appearing to congeal and having a sort of skin formed upon it. As soon as these signs are perceived, the crucible is covered, fresh charcoal supplied to the furnace, and the forge-bellows set in action; and as soon as the metal has become liquid, air is again blown upon it; the forge-bellows being meanwhile stopped, as in the first instance. But as the pellicle soon reappears upon the gold, the temperature must be again raised; and, in order more quickly to expel the antimony, the two bellows may be worked simultaneously, one to keep up the heat and the other to drive off the antimony. The gold still retains a little antimony, which is expelled by strongly re-heating the gold so as to make it very liquid; the gold ought now to appear limpid and without any cloud upon it, and, when this is the case, it is fine and malleable. But so long as any cloud is

[4] Lewis, op. antea cit. p. 157.

[5] I cannot suggest any reason for this.

ceived upon it, it contains antimony and is not malleable. The y is rendered less and less fusible by the expulsion of the imony, so that the heat should be much stronger during the ter part of the oxidizing process. However, if the temperature be high, there may be loss of gold by volatilization.[6]

Schlüter states that some persons, not finding the gold sufficiently ctile after its treatment by sulphide of antimony, re-melt it with tre or (? and) borax; but he adds, that they give themselves eedless trouble, because if, after the gold has been blown upon in he manner described, it be subjected to a "violent heat," so as to dissipate the cloud upon it caused by a small residue of antimony, very pure and very soft gold is obtained, and the cost of those salts is avoided. However, he goes on to state, when the gold is fine, a little calcined borax may be thrown into the crucible, as the gold may thereby be poured out cleaner; or, if considered expedient, it may be left to cool in the crucible.

When there is only a small quantity of the alloy of gold and antimony to operate upon, the latter may be removed by nitre, which should be added by very little at a time, because the mass easily rises and overflows. Three parts by weight of well-purified nitre to 1 part of gold suffice to render the gold very fine. The gold is mixed with the nitre and then put into the crucible, which should be heated gently at first and strongly at last, so as to make the gold very liquid and clean. If this treatment do not prove successful, it should be repeated with the addition of 2 parts of nitre to 1 part of gold.

The residual regulus consists of sulphide of silver and antimony, with sulphide of copper also, if that metal were present in the gold operated upon; and it contains a small quantity of gold. The silver may be extracted from it by several methods, as follows:—The surest method of recovering all the gold and silver is to drive off the whole of the antimony by means of a blast of air; but when there is much regulus to be treated, the labour is tedious and unhealthy; and yet, if it be desired that no gold should be lost, it is better to submit to that little inconvenience. If there be not much regulus, it may be melted in a Hessian crucible and blown upon in the manner described; or it may be heated on a large scorifier in an assay-muffle and then blown upon. But neither of those methods can be practised when there is much regulus; and in this case it is better to make use of a furnace such as is used in the refining of "blicksilber." A large flat scorifier, capable of holding 10 or 12 marks at a time, is placed in a bowl-shaped vessel of iron filled with wood-ashes, so that it may stand firm. Thus arranged, the scorifier is placed in the muffle, and gradually heated, the front of the furnace being closed with bricks;[7]

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[6] Macquer's Dictionary of Chemistry, English translation, 1771. 1. p. 587.

[7] For further information on this subject see the Author's volume on the Metallurgy of Lead.

and when it has become hot, the regulus is put into it and quickly melts. As soon as it is liquid and clear, the charcoal is removed from the mouth of the muffle, and a blast from the hand double-bellows is projected upon the molten regulus until the antimony is dissipated in smoke. When the fumes have ceased and the metal in the scorifier seems to be solidifying, the mouth of the muffle is closed with charcoal and the metal re-melted. The little remaining antimony evaporates, and the silver becomes extremely clear and nearly fine and is left to cool in the furnace.

When there is little regulus, and it is desired to save the time required for blowing, it may be melted in a Hessian crucible with its own weight of black flux, which is usually made of 2 parts of cream of tartar and 1 part of nitre. The contents of the crucible, which should be thoroughly melted and very clear, are poured into a conical mould, prepared in the manner previously stated, and, after cooling, the mould is inverted; when a lump of metal is obtained, which must be re-melted and blown upon to drive off the remainder of the antimony.

Another method of treating the regulus is to melt it in a Hessian crucible in a furnace, urged by a blast of air, and when it is well melted to throw in iron-filings by little and little until it will take up no more, which is ascertained by dipping an iron rod into the molten mass. After this, about $\frac{1}{2}$ oz. of granulated lead per mark of regulus is added, and the crucible strongly heated. The crucible is broken when cold, and the lump of metal is placed in a cupel; but it is necessary to blow again to drive off the metallic antimony, which has been reduced by the iron.

The silver separated from the regulus is cupelled with lead; but as it sometimes happens that such silver contains more than $\frac{1}{4}$ loth of gold per mark, it should be assayed for gold, and, if necessary, parted with nitric acid. According to Lewis, however highly gold may have been refined by antimony, it retains a little silver.[8]

With respect to the loss of gold in this process, the following statements are quoted from a paper communicated to the Royal Society by Dr. Jonathan Goddard in 1676.[9] Crown gold, 22 carats fine, was treated twice each time with 6 times its weight of sulphide of antimony. The alloy of gold and antimony was freed from the latter by a blast of atmospheric air in the manner above described. The plachmal was fused with tartar and nitre, and the metal reduced was also subjected to this treatment with a blast of air. The loss in fine gold was found to vary from 7·7% to 9·8%, and was supposed to have occurred partly during the pulverization of antimonial alloy rich in gold, partly in the sparks from the molten mass in the crucible, and partly, perhaps, in the fusion with tartar and nitre. The experiments were only on a very small scale.

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[8] Op. antea cit. p. 159.

[9] Experiments of Refining Gold with Antimony. Philosophical Transactions, 1676. 12. p. 953.

Summary of the process.—It consists of the following operations:—

I. Melting of the argentiferous gold, and adding thereto sulphide of antimony.

II. Re-melting the alloy of gold and antimony so formed, and separating the latter by atmospheric oxidation or otherwise.

III. Extraction of the silver from the sulphide of silver formed in No. I. by various methods.

SEPARATION OF SILVER FROM GOLD BY SULPHIDE OF ANTIMONY, AS FORMERLY PRACTISED IN THE ROYAL MINT AT DRESDEN.

For the following account of this process I am indebted to my friend Mr. J. Hochstätter Godfrey, to whom it was communicated by the Assayer of the Dresden Mint.

This method was in use at the Dresden Mint up to 1846, for the treatment of argentiferous gold.

The metal, which contains on the average 64·2 per cent. of gold, is melted in a covered Hessian crucible with the addition of about 3 times its weight of sulphide of antimony, an air-furnace being used for the purpose. As soon as the melted mass begins to emit sparks, it is poured out either into a conical iron mould or an old crucible; and to facilitate the settling of the metal from the resulting regulus, the mould or crucible is continually tapped until solidification takes place. A lump of gold alloyed with antimony is found at the bottom of the mass, and can easily be detached from the regulus above. This lump is re-melted with twice its weight of sulphide of antimony in the same manner as at first, and the lump from this second fusion is re-melted with an equal weight of the sulphide. By a preliminary assay of the lumps of metal deposited from these successive fusions, and which consist of an alloy of gold and antimony, the amount of gold retained by the regulus can be easily computed.

The whole of the regulus of the preceding operations is re-melted 3 or 4 times in Hessian crucibles, when small buttons of the alloy of gold and antimony are produced, which contain a considerable quantity of silver. To separate this silver, the alloy is re-melted with twice its weight of sulphide of antimony, and this process is repeated until the alloy yields gold of the desired fineness (= 993); namely, 23 carats 0 dwt. 10 grains, or 993 per 1000.

The various lumps of the alloy, which contain about 40 per cent. of antimony, are melted in a covered Hessian crucible, previously coated internally with powdered borax. As soon as fusion has occurred, this molten metal is exposed to a blast of air from a bellows, the nozzle of which is bent downwards. The antimony is by this means rapidly oxidized, and the resulting oxide blown off. When the whole of the antimony has thus been removed, the gold solidifies; nitre and borax, or nitre and corrosive sublimate, are then added, and the temperature is raised until the whole is melted. The resulting gold is then examined as to its fineness and ductility.

The regulus obtained from the previous operations, which chiefly consists of sulphide of silver with a little gold, is melted again in a Hessian crucible, with the addition of metallic lead, iron, and flux, when a lump of argentiferous lead is separated, which is cupelled. But as the regulus and slag associated with the lump contain a considerable quantity of silver (about 1000 ozs. to the ton), they are smelted along with the "sweep" of the Mint. From 25 to 30 marks of the argentiferous lead are cupelled at a time, and the resulting silver, being auriferous, is broken into pieces, melted, granulated, and parted by nitric acid. The silver is precipitated from the nitrate solution by metallic copper and melted with the addition of carbonate of soda; but, previously, the excess of nitric acid is partially separated by distillation and condensed. The gold is rendered fine by melting it with the addition of borax and nitre.

The cost of this process amounts to 15 ngr. (1*s*. 5½*d*.) per mark of argentiferous gold operated upon, the price of the sulphide of antimony being estimated at 14 thalers per centner (=£2 4*s*. per cwt.).

The disadvantages of the process are that it is more expensive than parting by sulphuric acid, and that there is formed a considerable quantity of regulus rich in silver, which retains a little gold.

SEPARATION OF SILVER FROM GOLD BY SULPHUR AND COPPER.

This process has for its object the partial separation of silver from an alloy of gold and silver consisting chiefly of the latter: it was practised in the Mint at Delhi in the 16th century, and is described in the Institutes of Akbar, written in Persian, of which there are two translations into English, one by Gladwin, published in 1800,[1] and the other by Blochmann, published in 1873.[2] In preparing the following account, as well as that to be subsequently given of other processes described in the same book, I have availed myself of both translations; and have also had the assistance of a well-educated Persian, Mirza Mehdy Khán (now in England, 1878), who translated to me the description from the original Persian, and detected certain errors in the translations above mentioned, making some points clear which in those translations are obscure. I have much pleasure in acknowledging the assistance which I have thus received.[3]

"They melt this composition six times; three times with copper, and three times with *sulphur*, called in Hindí *chhachhiyá*. For every

[1] Ayeen Akbery; or the Institutes of the Emperor Akber. London, 1800. 1. pp. 18, 19.

[2] The AIN I AKBARI. By Abul Fazl 'Allami, translated from the original Persian by H. Blochmann, M.A., Calcutta Madrasah. Calcutta, 1873. 1. pp. 25, 26.

[3] The following descriptions within inverted commas are from Blochmann (pp. 25, 26), and Mirza Mehdy's alterations are interpolated within brackets.

ah of the alloy, they take a máshah of copper, and 2 máshahs urkhs of sulphur (see table of weights in the note).[4] First, they lt it with copper, and then with sulphur. If the alloy be of 100 ahs weight, the 100 máshahs of copper are employed as follows:— ey first melt 50 máshahs with it, and then twice again, 25 máshahs. he sulphur is used in similar proportions. After reducing the ixture of gold and silver to small bits, they mix with it 50 máshahs f copper, and melt it in a crucible. They have near at hand a vessel ll of cold water, on the surface of which is laid a broom-like bundle f hay [twigs]. Upon it they pour the melted metal, and prevent it, y stirring it with a stick, from forming into a mass. Then having gain melted these bits, after mixing them with the remaining copper in a crucible [these granules are mixed with half of the other ingredient (*i.e.* sulphur), placed in fire and melted], they set it to cool in the shade: and for every tólah of this mixture [*i.e.* original alloy], 2 máshahs and 2 surkhs of sulphur are used, *i.e.* at the rate of 1 and ½ quarter sér (1⅜ sér) [1 quarter and ½ quarter, *i.e.* ⅜, and not 1⅜] *per* 100 *tólahs*. [The fraction of the sér here stated does not agree with that computed from the weights in the table.— J.P.]. When it has been three times melted [treated] in this manner, there appears on the surface a whitish kind of ashes, which is silver. This is taken off and kept separate; and its process shall hereafter be explained. When the mixture of gold and silver has thus been subjected to three fires for the copper, and three for the sulphur, the

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[4] The present Indian tólah dates from 1833, and is 180 grains, as will be seen in the following table of Indian weights:—

Surkh or rati *	= 1·875 grain.
8 surkhs = 1 máshah	= 15 grs.
12 máshahs = 1 tólah	= 180 grs.
80 tólahs = 1 sér	= 2·057 lbs. (Avoirdupois).
40 sérs = 1 mán	= 82·28 lbs. (id.) = 100 lbs. (Troy).

* Mr. Thomas informs me that "surkh" is Persian for "red," that the weight is derived from the red seed of the leguminous plant *Abrus precatorius*, and that "rati" is another name for the same weight.

I have consulted my excellent friend Mr. Edward Thomas. F.R.S., on the very difficult subject of ancient Indian weights,—on which there is no higher authority,—and have received from him the following interesting note:—

"The old *rati*, the seed of the *Abrus precatorius*, was estimated, in the normal Hindu system, at 1·75 grain. They had a *silver* másha made up of 2 ratis, and a *gold* másha made up of 5 ratis. The latter estimate also applied to copper; so 80 *ratis*, or 140 grains, constituted the weight called *Suvarna*, which was the prototype of the later gold and silver money.

"When the Moslims came to India, they revived an ancient 100 rati weight; and hence their 'Tankas,' both for gold and silver, ran at 175 grains. The earliest examples of these appear under Sultán Altamsh (A.D. 1210–1235). 'Alá ud dín, Muhammad Sháh (1295–1315), reduced his coins to the old 140 grains, in order to delude his army by paying by number, instead of by weight. We need not follow the modifications introduced by successive kings, but come to the time referred to in the text. Shír Sháh, from whom Akbar took so many notions (unacknowledged), made his 'rupee'—now so called for the first time—92 ratis or 11½ máshas, equal, as I make it, to 178·25 grains. The rati being therefore 1·9375 grain, Akbar increased the weight of the tolah to 96 ratis or 186·0 grains. It must be understood that the tangible *rupee*, or silver coin, was the representative of the official *tolah*, and *the unit* of the entire system of weights. (March 23, 1878)."

solid part left is the gold. In the language of the Panjáb, this gold is called *kail*, whilst about Dihlí [usually spelt Delhi] it is termed *pinjar*. If the mixture contained much gold, it generally turns out to be of 6½ *bán* [*i.e.* 6½ parts by weight in 12 parts], but it is often only 5, and even 4.

"In order to refine this gold, one of the following methods must be used:—Either they mix 50 tólahs of this with 400 tólahs of purer gold, and refine it by the *Salóní* process; or else they use the *Alóní* process. For the latter they make a mixture of 2 parts of wild cow-dung, and 1 part of saltpetre. Having therefore cast the aforesaid *pinjar* into ingots, they make it into plates, none of which ought to be lighter than 1½ tólahs, but a little broader than those which they make in the *Salóní* process. Then having besmeared them with sesame-oil (*i.e.* a fixed oil like olive-oil), they strew the above mixture over them, giving them for every strewing two gentle fires. This operation they repeat three or four times; and if they want the metal very pure, they repeat the process until it comes up to 9 *bán* [*i.e.* 9 parts of gold by weight in 12 parts, or 75 per cent.]. The ashes are also collected, being a kind of *k'haral*.

"*The Method of extracting the Silver from these Ashes.*—Whatever ashes and dross have been collected, both before and after the process of *Alóní*, they mix with double the quantity of pure lead, put them into a crucible, and keep them for one watch [*i.e.* 3 hours] over the fire. When the metal is cold, they refine it as described under the article *Sabbák*. The ashes of it are also *k'haral*. The Salóní process is also performed in other ways, well known to those conversant with the business."

The alloy, subjected to the treatment above described, consisted chiefly of silver, as may be inferred from the statement, that after such treatment the residual metal contained only from ⅓ to about ½ its weight of gold; and that when it was desired to make it richer in gold, it had to be cemented with nitrate of potash. The object, then of this process was, as previously stated, the partial separation of silver from an alloy of gold and silver in which the latter greatly preponderated.

The proportions, by weight, of alloy, copper, and sulphur used are nearly as follow: 12 : 1 : 2·25. The proportion of sulphur is nearly 9 times as much as is theoretically required to convert the whole of the copper into cuprous sulphide, so that after this conversion is effected there remains sufficient sulphur to form a comparatively large quantity of sulphide of silver; 2·25 parts, by weight, of sulphur suffice to convert 1 part of copper into cuprous sulphide and 13·5 parts of silver into argentic sulphide.

According to Blochmann's translation, the alloy was first melted with half of the copper, and the resulting metal was granulated; the granulated metal was re-melted with half of the remaining copper and granulated; and this granulated metal was re-melted with the other half of the remaining copper and again granulated. But such a method of procedure is quite unintelligible; for the alloying of the original

auriferous silver with the copper might have been as certainly effected by one fusion as by three. The correction, however, of this part of Blochmann's translation by Mirza Mehdy tends to remove some of the obscurity: thus, according to that correction, the granulated alloy was re-melted with sulphur and copper *alternately*. Nothing, however, is stated with respect to the regulus formed in the first two fusions with sulphur; and the question, therefore, arises whether it was removed after each of those fusions. Either of the two following methods might have been adopted: one is, fusion of the granulated alloy of auriferous silver and copper with sulphur; separation of the regulus formed; re-melting the lump of metal with copper, re-granulating the resulting alloy and re-melting this granulated metal with sulphur; and a similar and last repetition of these successive operations: the other method is the same, except that in each fusion the previously formed regulus constitutes part of the ingredients. But it is distinctly mentioned that there were three fusions with copper and three with sulphur, six in all; but, if the regulus had not been removed after each fusion with sulphur, what, it may be asked, could have been the reason for allowing the molten mass after each fusion with sulphur to become cold and solidify? Is it possible that, assuming the regulus to have been removed after each of the first two fusions with sulphur, the re-melting of this regulus along with the granulated cupriferous alloy and sulphur might have had for its object the separation of gold from the regulus (see the preceding article on the Separation of Gold from Silver by Sulphur, p. 358)? There must, presumably, have been some good reason for the use of copper in this process, but what that reason was can only be a matter of conjecture in the absence of experimental evidence on the subject.

In the last operation, it is stated "there appears on the surface a whitish kind of ashes, which is silver;" and, doubtless, the statement is correct. The occurrence of metallic silver under similar conditions has been previously mentioned in this volume (p. 364). The theory of the mode of extracting the silver from the regulus described at p. 376 is so obvious as not to need elucidation.

The use of copper, in conjunction with sulphur, for the separation of silver from silver containing gold is mentioned by Perez de Vargas,[5] and by Alonzo Barba who thus describes the process. The silver is granulated, and well mixed by trituration with 2¼ ozs. of sulphur to 12 ozs. of silver. The mixture is heated in a "new earthen pot thoroughly luted" in what is called a "wheel-fire" (that is, a fire made at a little distance round the crucible), in order that by a gentle heat the sulphur may unite with the silver without igniting: such a mode of heating is also mentioned by Agricola and Perez de Vargas, and by Schlüter in his account of the cementing of silver with sulphur, who states that the diameter of the circle of fire is at first about 3′, and that it is gradually

[5] Traité singulier de Métallique. Paris, 1743. 2. pp. 33–42.

diminished until at last the fuel is in contact with the crucible (op. antea cit. 2nd part, p. 166). The silver, now quite black, is withdrawn from the crucible, and mixed with half of the total weight of the granulated copper used in the process; namely, 3½ ozs. to every 12 ozs. of original silver. The mixture is heated in a covered crucible until the whole is melted, and to the molten mass is added a spoonful of granulated copper and another of a mixture made of equal parts of litharge in small particles (*petits morceaux*), and "glass-gall" (*i.e.* the saline matter which comes to the surface in what is technically termed "founding" at glass-works). The crucible is again covered; and when the whole is melted, the remaining granulated copper and the mixture above described are added by spoonfuls. "The gold falls to the bottom, and the silver remains above, mixed with lead, copper, and sulphur." The molten contents are poured into an ingot-mould, when "the gold will separate easily from the composition (*plachmal*), which is very brittle. Before taking the crucible out of the fire, a little of the composition is withdrawn and refined with the addition of lead on a test, and the resulting silver is dissolved in nitric acid. By this means it is seen whether the gold has been sufficiently separated or not; if not, the fire is continued."[6]

The quantity of sulphur theoretically required to convert 12 ozs. of silver into sulphide is 1¾ oz.; but as an excess of only ¼ oz. was used, and as some of the sulphur was probably volatilized, it is doubtful whether the silver was completely sulphurized. Combination of the silver with sulphur seems to have been effected below the melting-point of sulphide of silver. The quantity of copper used required for its conversion into cuprous sulphide about ¾ oz. of sulphur; so that, supposing the silver to have been changed into sulphide, there was not nearly sufficient copper to remove the whole of sulphur from that sulphide. But as litharge was added, the weight of which is not stated, part of the sulphur would be removed by that substance, not however without the separation of some metallic lead. Yet it is asserted that "the gold falls to the bottom;" but if *pure* gold be meant, I cannot satisfactorily account for the fact.

Homberg communicated a process to the French Academy in 1701, by which he proposed to separate copper from silver by means of sulphur and iron. The alloy of silver and copper is melted with the addition of half its weight of sulphur; and when the whole is molten, iron filings are added at intervals in suitable quantity which, he says, may be easily determined during the operation. The silver is precipitated and forms a button at the bottom of the crucible, while the copper remains in the regulus.[7] But it is hardly necessary to remark, that it would not be easy to judge concerning the proportion of iron requisite; and that if too much were added

[6] Metallurgie, ou l'Art de tirer et de purifier les Métaux, traduite de l'Espagnol d'Alphonse Barba. A la Haye 1752. I. p. 382.

[7] Idem, 2. p. 394.

copper would be precipitated along with the silver. Further information on this subject will be found at page 157 of this volume.

SEPARATION OF SILVER FROM GOLD BY CEMENTATION WITH NITRATE OF POTASH.

The object of this process is the separation of silver from argentiferous gold, and the following account of it as practised in the Mint at Delhi, in the reign of Akbar, has been derived from the same sources as those mentioned in the article on the Separation of Silver from Gold by Sulphur and Copper.

The melter of the ore makes small and large furrows in a slab of clay, which he smears with grease, and pours into them the melted gold and silver, and leaves them to solidify. For copper, instead of using grease he sprinkles the moulds with ashes. The plate-maker makes the impure gold into plates of the weight of 6 or 7 máshahs each, and 6 fingers square (*i.e.* about 4½ inches): these he carries to the assay-master, who measures them in a mould made of copper, and stamps such as are found correct, in order to prevent alterations, and to show the work done. When the plates have been stamped, the owner of the gold, for the weight of every 100 jaláli goldmuhurs, must furnish 4 sérs of saltpetre, and 4 sérs of unburnt brickdust. [The L'al Jaláli was 1 tólah 0 máshah 1¾ rati in weight of gold; in value 400 dáms or 10 rupees.—E. Thomas.]

The plates, after having been washed with clean water, are coated with the above mixture, and put one above the other, and the whole is surrounded with dry cow-dung from the fields.[8] They then set fire to it, and let it burn gently, till the cow-dung is reduced to ashes, when they leave it to cool; then these ashes, being removed from the sides, are preserved in order that the silver which they contain may be extracted. These ashes are called in Persian *khák i khaláç*, and in Hindí *salóní*. The plates and the ashes below them are left as they are. This process of setting fire to the dung, and removing the ashes at the sides, is twice repeated. When three fires have been applied, they call the plates *sitái* (which means three times treated). They are then again washed with clean water, and stratified three times with the above mixture, the ashes being removed from the sides.

This operation must be repeated, till six mixtures and eighteen fires have been applied, when the plates are again washed. Then the assay-master breaks one of them; and if there comes out a soft and mild sound, it is a sign of its being sufficiently pure; but if the sound is harsh, the plates must be coated with the mixture once again, and passed through three more fires. Then from each of the plates is taken 1 máshah, of which aggregate a plate is made and tried on

[8] Blochmann translates it dung of the wild-cow, which Mirza Mehdy says is not correct. Mr. Thomas informs me that it is cow-dung from the jungle. The reason for preferring dung from fields is because it is purer than that from stables in towns, which is apt to be mixed with rubbish of various kinds.

the touchstone; and if it is not sufficiently fine, the gold has agai pass through one or two fires. In most cases, however, the des effect is obtained by three or four fires.

The following method of testing the quality of the gold is also u They take 2 tólahs of pure gold and 2 tólahs of the gold w has passed through the fires, and make 20 plates of each, of e weight. They then spread the above mixture evenly, and apply fire, wash them, and weigh them with an exact balance. If kinds are found to be equal in weight, it is a proof of pureness. gold thus refined is melted and cast into ingots.

Treatment of the ashes.—The ashes (*khák*) are washed, 2 sérs time; and whatever intermixed gold they may contain, will, its weight, settle to the bottom. The impure sediment is tritu with quicksilver, in the proportion of 6 máshahs per sér. quicksilver from its friendly attraction draws the gold to itself this (*i.e.* the amalgam) is put into a glass vessel, and the separated by means of fire.

They mix with the washed ashes (*kukrah*) an equal quanti *punhar* (*i.e.* the name given to a test made of wood-ashes, on v argentiferous lead has been refined, and which is therefore ch with litharge), and form a paste of *rasí* (aquafortis)[9] and field dung. They then pound the first mixture (*i.e.* of ashes and *pu* and, mixing it with the second (*i.e.* the paste), work it up into of 2 sérs in weight, which they dry on a cloth. They make a l earthen oven-like vessel, with two narrow ends, and wide in middle, 3 hands high (a hand is the length from the elbow to th of the middle finger, and is about 16 inches), with a hole at the bo Then having filled the vessel with charcoal within four fingers c top, they place it with the bottom hole over the centre of a pi in the earth, and make a fire all round it, and blow with bel (This vessel, as far as I can interpret the description, seems to been more or less pear-shaped, with a hole at the top and an at the bottom.) When the vessel is red-hot, the balls having broken into pieces, are thrown into the vessel and melted; the silver, copper, and lead fall through the hole in the bottom o vessel into the pit below. Whatever remains in the vessel is out, kneaded with water,[1] and then washed, whereby the le separated from it. They likewise collect the ashes, from which by a certain process a profit is gained. The metal is taken out c pit and refined by the *punhar* method (*i.e.* cupelled on a test of ashes). The lead will mix with the ashes (*i.e.* the litharge pro will be absorbed by the test), from which 30 sérs will be reco

[9] In Gladwin's translation, it is stated to be made from soap-ashes—*i.e.* lixiviated wood-ashes — and saltpetre earth. By heating a mixture of those substances nitric acid would be evolved, the silica of the ashes combining with the potash of the saltpetre earth, and so setting free the acid. In Blochmann's translation, "*rasí* is stated to be a kind of acid of *ashkhar* and saltpetre;" and in it is further stated that some of the explain this word by *sijji*, Hindoo word for impure carbonate of soda.

[1] The word "softened" is in mann's translation, but not in Gla

and 10 sérs will be burnt (or lost, as will be easily understood by persons acquainted with the metallurgy of lead). The gold, silver, and copper, with a small quantity of lead, will remain together in a mass; and this they call *bugráwati*, or, according to some, *gubráwati*.[2]

The metallic mass from the last operation, *bugráwati*, is treated by a method of cupellation, the description of which in Blochmann's translation is as follows:—They make a hole and fill it with the ashes of *babúl*-wood (*Acacia Arabica*), half a sér for every 100 tólahs of *bugráwati*. These ashes they then make up in form of a dish, and fill it with *bugráwati*, adding 1 tólah of copper and 25 tólahs of lead. They now fill the dish with charcoal, and cover it with bricks. When the whole has melted, they remove the charcoal and the bricks and make a fire of *babúl*-wood, till the lead and copper unite with the ashes, and the mixture of gold and silver separates. These ashes are called *k'haral*, and the lead and copper can be recovered from them by a particular process. The *k'haral*, I infer, is the test charged with litharge.

The *k'haral* is broken into small pieces, and to every mán (formerly spelt maun = 40 sérs) of it, 1½ sér of *tankar* (tincal or borax) and 3 sérs of pounded natrum (carbonate of soda?) are added, and all the ingredients are kneaded together. This mass is then put, sér by sér, into the vessel previously described, and melted, when the lead mixed with silver drops through the hole at the bottom into the pit; and the argentiferous lead is cupelled in a test of wood-ashes.

The *Paikár* or peddler buys the *salóní* and *k'haral* from the goldsmiths of the city, and carries them to the mint to be melted, and makes a profit on the gold and silver. For every mán of *salóní*, he gives 17 dáms (100 dáms = 2½ rupees); and for the same quantity of *k'haral*, 14 dáms to the exchequer.

When the owners of the metals get their gold and silver by the various processes practised at the mint, and which are all described in the translations, the Khakshóe or washer of ashes sweeps the mint, takes the sweepings to his own house, washes them, and gains a profit. Some of the sweepers carry on a very flourishing trade. The State receives from this man a monthly gift of 12½ rupees. And in like manner all the officers of the mint pay a monthly duty to the State, at the rate of 3 dáms for every 100 dáms.

All the artificers of the mint appear to have been paid on the piece-work system.

An account of the process of separating silver from gold by cementation with nitre, in admixture with pounded brick and other substances, of which may be mentioned chloride of ammonium and ferrous sulphate, is given by Agricola, Perez de Vargas, and others. The construction of the furnace and the mode of conducting the operation are described at considerable length; and it is stated that

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[2] The last sentence is given literally from Gladwin's translation; but in Blochmann's it is as follows:—The gold, silver, and copper remain together in a mass. I should think it very probable that lead was present, as Gladwin states.

the argentiferous gold may be used in the granulated as well as in the laminated form.[3]

The following description of the process of cementing argentiferous gold with nitrate of potash is given by Lewis[4]:—"Though the nitrous acid in its liquid state does not extract silver from gold unless the quantity of silver greatly exceeds the gold; yet in cementation, where the acid, resolved into fumes, is applied to the metal at the same time strongly heated, it attacks and corrodes a part of the silver, though its proportion be very minute. For this purpose nitre in substance is mixed with equal its weight of common green vitriol calcined, or dried as for the making of aquafortis, and with twice its weight of powdered bricks; the one to extricate the acid when sufficiently heated, and the other to prevent the mixture from growing fluid in the fire. The metal is flatted into thin plates which are surrounded and interlaid with this powder, in a crucible or in an earthen vessel made on purpose for this use, called a cementing pot: the vessel is closely covered, and the juncture secured with a mixture of soft clay and sand, or other proper clayey compositions and being placed in any convenient furnace, a moderate heat is kept up for twelve or sixteen hours. The silver, and most of the base metals along with it, are corroded by the nitrous vapour into a saline concrete, which partly adheres in the pores of the gold, and is partly dispersed through the mixture. From the gold, the corroded silver may be boiled out with water, and afterwards recovered from the liquor in the same manner as from its solution in aquafortis: from the mixture, it is much more difficultly extracted, by boiling the matter in melted lead, and afterwards working off the lead, into which the silver has thus transferred itself, upon a cupel or test. The quantity of silver, however, which cementation is employed for separating from gold, is commonly so small as to be entirely disregarded. The acid of sea-salt, applied in the same manner, corrodes all the metallic bodies except gold or platinum. Hence either sea-salt or nitre may be used in this process indifferently; but they must never be taken together, as some have directed them to be, for the two acids in conjunction would dissolve the gold itself. . . . . The gold plates cannot be wholly freed from their alloy by one operation, either with the nitrous or marine cements, the vapours penetrating but very little way into their substance. Hence for the effectual purification of gold by this method, the metal is to be re-melted, flatted into plates, and again exposed to the fumes. The process indeed appears incommodious upon the whole, whether considered as a method of purifying gold or of ascertaining its purity; and accordingly, though once in much esteem, it is now rarely practised. Its principal use is for extracting silver or base metals from the surface of gold, and thus giving superficial purity and high colour to alloyed or pale gold."

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[3] Traité singulier de Métallique. Paris, 1743. 2. pp. 48–60.

[4] Commercium Philosophico-Technicum, pp. 154, 155.

Ercker mentions nitrate of potash as an ingredient of some of the cementing powders, of which he gives the composition. One of these mixtures consists of 16 loths of the "powder of an old dry tile (not too hard burnt, neither too sandy)," 8 loths of salt, 4 loths of white vitriol, 1 loth of saltpetre, and 1 loth of verdigris; and another mixture consists of 14 loths of tile-powder, 4 loths of hæmatite, 1 loth of *crocus martis* (peroxide of iron), 1 loth of verdigris, 6 loths of white vitriol, and 3 loths of saltpetre.[5] The "white vitriol" is stated to have come from Denmark;[6] but whether by this term was meant alum, sulphate of zinc, or simply green vitriol (ferrous sulphate) which had been heated so as to drive off water of crystallization and thereby made white, I do not know. Sulphate of zinc does not evolve sulphuric acid when it is decomposed by heat, but only a mixture of sulphurous acid and oxygen, and would therefore appear to be useless in the process, as it would not, like alum or ferrous sulphate, set free nitric acid from the nitrate of potash.

Silver crucibles are, as is well known, recommended to be used in chemical analysis, for fusions with nitrate of potash, under the impression that silver is not attacked by the molten salt as platinum would be; but, in using silver crucibles for this purpose, I have found that the metal is attacked in a very sensible degree, and that when the melted mass, after cooling, is put into water, oxide of silver is left undissolved. The extraction of silver in the process of cementation with nitrate of potash, is due, it is presumed, to the formation of nitrate of silver, and its absorption, while molten, by the surrounding porous cementing powder. It seems probable that the saltpetre used in former times may have often contained a considerable quantity of common salt; but what the precise chemical reactions may be during cementation with a mixture of those salts I am unable at present to state. My friend Mr. Abel, Chemist to the War Department, informs me that he has not succeeded in obtaining any evidence that chlorine is evolved when a mixture of nitrate of potash and chloride of sodium is heated in the presence of the vapour of water. The reason assigned by Lewis for not using a mixture of these two salts is, that the gold would in that case be attacked and dissolved; and if chlorine were evolved under the conditions above stated, there is reason to believe that although chloride of gold cannot exist *per se* at the temperature at which cementation is conducted, yet that it may, when associated with chloride of silver, exist at that temperature. Evidence to this effect will be found in the sequel in the article on Miller's process of separating silver from gold by passing a stream of chlorine through the molten metal.

The mention by Ercker of the use of verdigris in conjunction with common salt and saltpetre in the cementing mixtures deserves particular notice, because in Deacon's newly-invented process chlorine is obtained by passing a mixture of hydrochloric acid vapour and

[5] Fleta Minor. London, 1686 pp. 209, 210.
[6] Idem. The second part, p. 128.

atmospheric air through pounded brick impregnated with sulphate of copper. Deacon asserts that copper salts possess this power in a very marked degree, and that all the compounds of copper which he had tried proved to be equally active;[7] but whether acetate of copper or verdigris was one of them is not stated. However, hydrochloric acid would be evolved from the cementing mixtures, containing verdigris, and convert it either partially or wholly into chloride of copper, which Deacon, doubtless, had tried. Thus chlorine was probably produced more than three centuries ago in the same manner as in Deacon's process; and if so, it is conceivable that the reading of this account in Ercker's treatise might have suggested experiments to ascertain why verdigris was employed, and have led to the discovery of the generation of chlorine on the principle of that process.

SEPARATION OF SILVER FROM GOLD BY CEMENTATION WITH CHLORIDE OF SODIUM.[8]

This is a "dry" process, of which the object is the purification or refining of gold containing small proportions of silver, copper or other base metal; and, by way of introduction, may here be appropriately inserted the following remarks of Savot, in his "Recherches sur la Métallurgie des Anciens," published early in the 17th century.[9] In this process the separation of "gold from silver, or copper from these two latter metals,[1] is effected by means of a composition called royal cement, which is made of bricks reduced to fine powder, and of other substances having a special property of acting upon silver as well as copper without injuring gold, and of withdrawing and separating from gold all the silver and copper alloyed with it without producing any change in the articles acted upon by the cement, except that of rendering the gold very beautiful, very pure, and very high (*très-haut*) in colour, and decreasing the weight of those articles by the amount of silver and copper which they contained. In this operation,

[7] Chemical News, Sept. 30, 1870.

[8] The word cement is derived from the Latin *cæmentum*, one meaning of which is stated to be small pieces or chips which fly off in the cutting of stone or marble. Thus *cæmenta marmorea* means chips of marble. (See Smith's Latin Dictionary.) The definition of the word, as used by metallurgists, in Webster's Dictionary, is as follows:—"A process which consists in surrounding a solid body with the powder of other substances, and heating the whole to a degree not sufficient to cause fusion, the physical properties of the body being changed by chemical combination with the powder; thus iron becomes steel by cementation with charcoal, and green glass porcelain by cementation with sand." The last example in illustration of the definition is not appropriate; for, in the case in question, the sand is absolutely inert, and not a particle of it enters into combination with the glass. In Hellot's French translation of Schlüter two meanings are given of the word *cément*: one is the mudlike deposit of copper precipitated from a solution of sulphate of copper by iron; and the other is a reservoir in which the copper solution is collected for precipitation by iron. (De la Fonte des Mines. Paris, 1753. 2. p. 508.)

[9] Les Anciens Minéralogistes du Royaume de France; avec des Notes. Par M. Gobet. Paris, 1779. p. 850.

[1] "Le second moyen de separer l'or d'avec l'argent, ou le cuivre d'avec ces deux derniers metaux etc." This is obscure; because copper cannot, as is stated, be separated from silver by this process.

ough the gold may be alloyed with only a very small quantity of er or copper, yet this cement does not fail to act however small t quantity of silver and copper may be, whereas nitric acid has no ion if the gold be not alloyed with at least twice its weight of er or copper."

The cementing mixture was called royal because it was used to rify gold, which the alchemists designated the king of metals.

The earliest mediæval description of the purification of metals by rocess of cementation that I have met with is contained in Latin atises said to be translations of those in Arabic by Geber, who is ieved to have lived in the eighth or ninth century. It should, wever, be stated that Beckmann, the learned author of the "History Inventions," held the opinion that such translations were probably t of earlier date than the twelfth century. (See the article in the uel on Parting by Nitric Acid.) In a chapter on the properties of ld in one of these translations occurs the statement that it supports test of cupellation and *cementation:* the words are "cineritii et menti tolerans." (Alchemiæ Gebri Arabis philosophi solertissimi bri etc. Joañ: Petreius Nurembergeñ. denuo Bernæ excudi faciebat. no 1545. p. 51.) The same volume contains the following account the process of cementation (p. 155). The ingredients of the menting mixture are "vitriolum, sal ammoniacum, et æris flos, et pis fictilis antiqui contriti [in another translation from a MS. in the atican, entitled Gebri Regis Arabum philosophi perspicacissimi. edani, 1682. p. 186, it is "lapis figuli antiquus, contritus"], et lphuris minima quantitas, aut nihil, et virilis urina, cum similibus utis, et penetrantibus. Incementantur igitur hæc omnia cum urina rili, et super corporis illius tabulas tenues ponuntur, de cujus tentione sit probationis examinari judicio. Dehinc vero tabulæ nclusæ in fictili vase extendantur super cratem ferream, ita tamen, od una ex eis alteram non tangat, ut libere ignis virtus ad illas rcurrat æqualiter, et sic triduo in igne forti conservetur fictile. utela tamen adhibeatur, ut igniantur tabellæ, sed non fundantur. st tertiam autem diem tabellas omni impuritate mundas invenies, in perfectione illarum extiterit corpus. Si vero non, corruptas nino et calcinatione combustas. Quidam tamen, ponunt ad inflam-tionem tabellas, absque compositionum cemento, et depurantur niliter, si perfectionis sint corpora. Si vero non, comburuntur nino. Longiori tamen combustionis spacio in hoc ultimo egent amine, quod sola ignis inflammatione perficitur, quam quæ cementi aminantur judicio."

The translation is as follows:—The ingredients are "vitriol rrous sulphate), sal-ammoniac, flower of copper (scale of oxide of pper formed by heating the metal with access of air. See Pliny, t. Hist. lib. xxxiv. cap. xi. sect. 24, Sillig's edition), ground old rthen pot, sulphur in the smallest quantity or none at all, man's ine, together with similar sharp and penetrating substances. All ese things with man's urine are placed upon thin plates of the bstance, which it is intended to test, and cemented. But the

plates, inclosed in an earthen vessel, are spread out on an iron grating, so that one may not touch the other in order that all may be freely and equally exposed to the heat, the vessel being kept in a strong fire during three days. Care, however, should be taken to heat the plates without melting them. After the third day the plates will be found to be cleansed from all impurity, if the substance of them had existed in a state of perfection. [The metals, for example, were considered to be compounded of the same elements, and their substance to vary in perfection, according to the proportions of those elements, gold being the only perfect metal.] But if not, they will be wholly consumed and burnt away by the calcination. Some persons, indeed, subject the plates to fire without the cement compound, and they are similarly purified, if their substances be in a state of perfection. But if not, they are wholly consumed. A longer period, however, is needed in this method, which is effected by the sole action of fire, than in that of cementation." I do not understand that part of the description in which it is clearly stated that the plates are spread out on iron gratings *within* the closed earthen vessels; and I suspect that the original passage in Arabic has been mistranslated. The ground of this suspicion will be seen in Biringuccio's account of the cementation process, in the sequel. Although common salt is not mentioned as one of the ingredients of the cementing mixture, yet it exists in urine, and a substitute for it would be produced by the action of the vitriol (ferrous sulphate) on the sal-ammoniac (chloride of ammonium), chloride of iron. The theory of the process will be evident from what is stated on this subject in the sequel.

This cementation process is probably very ancient; but, as the evidence on this point cannot be properly considered before the process has been described, it will be given at the end of this article. Although it is now obsolete, except in Japan and perhaps in some localities in the East or in South America, yet, as it is exceedingly interesting in a metallurgical point of view, I shall consider it at length, and not despatch it in such a summary fashion as Karsten has done in his "System der Metallurgie." I hold it to be important to describe many processes which have been abandoned, because, without a knowledge of them, it would not be possible to trace the development of the metallurgic arts, one of the objects which I have in writing these volumes, and one full of interest to every one not wholly absorbed in the present. Moreover, the study of the past in this branch of knowledge teaches, that the old metallurgists showed much inventive power in their processes, much skill in their manipulations, marvellous patience, indomitable perseverance, and were not so ignorant as some modern metallurgists imagine; that information of practical value may even now be derived from the careful study of various obsolete processes; and that waste of time and money in profitless re-invention may possibly be thereby prevented. And it might also be added that the perusal of the treatises of the old metallurgists may suggest improvements even in existing processes.

This process was known to Albertus Magnus, who lived in the 13th century, and his description of it is as follows:—"Cum autem aurificari debet aurum, fit testeum vas ad modum cucurbitæ vel cutellæ factum, et super illud vas simile illi, et conglutinantur in loco contractuum (*sic*), et tenaci luto quod sapientiæ lutum vocant alchimici. In superiori autem sunt foramina multa per quæ exeat vapor et fumus, et postea attenuatur aurum in laminas breves et tenues, et ordinantur in vase, ita quod quilibet ordo laminarum subtus, et supra habeat pulverem fuliginis, et salis, et lateris farinati commistorum, et decoquitur in igne forti donec purissimum est, et consumuntur in eo substantiæ ignobiles. Lutum autem sapientiæ de quo fiunt testæ fit ex testa contrita et iterum commista, et decocta, hoc enim vas in igne positum comminuitur igne sensibili consumtione. Tamen alio modo in alchimicis præparatur lutum sapientiæ, sed illud hic sufficiat quo aurifices utuntur. Sic igitur purificatur aurum, et non exuritur in eo nisi substantia ignobilis." (De Mineralibus et Rebus Metallicis. Coloniæ, 1569, lib. iv. p. 360. Some apparently typographical errors in the original have been corrected.)

The following is a free translation of the above description in Latin:—"But when gold is to be purified, an earthen vessel is made like a cucurbit[2] or dish, and upon it is placed a similar vessel; and they are luted together with the tenacious lute called by alchemists the lute of wisdom. In the upper vessel there are numerous holes by which vapour and smoke may escape; afterwards the gold, in the form of short thin leaves, is arranged in the vessel, the leaves being covered consecutively with a mixture obtained by triturating together soot, salt, and brickdust; and the whole is strongly heated until the gold becomes perfectly pure, and the base substances with which it was mixed are consumed. The lute of wisdom, from which 'testæ' [*têts à rôtir?* of the French, clay roasting dishes] are formed, is made of a baked mixture of pounded burnt earthen vessels [and raw clay?], as the vessel contracts in the fire and perceptibly wastes. There is, however, another method prescribed in alchemical writings for making this lute; but that here given, which is used by goldsmiths, may suffice. So gold, therefore, is purified, and only the base part in it is burnt away." The passage relating to the lute of wisdom in which the word "testæ" occurs, is obscure, and the translation of it which I have presented is to a certain extent conjectural.

The earliest and most detailed account of this process which I have seen is that in Biringuccio's treatise, published at Venice in 1540;[3] and of that account I present the following abstract:—The furnace

[2] "A cucurbit is a chemical vessel employed in distillation, when covered with its capital or head. Its name comes from its longthened shape, by which it resembles a gourd: some cucurbits, however, are shallow and wide-mouthed." (Macquer's Dictionary of Chemistry. London, 1771. 1. p. 194.)

[3] De la Pirotechnia. Book iv. chap. 7, folio 72. Modo di cimentare l'Oro et di condur lo a l'ultima sua Finezza.

consists of a chamber [rectangular, according to Agricola and Ercker], having an iron grate about half a braccia (1 foot English ?) from the ground, and one or two square iron bars of the width of a finger or more stretching across, at the height of a braccia above the grate.[4] The furnace is open at the top, and has no chimney; and there is an opening at the bottom on one side for introducing the fuel and for the entrance of the air under the grate. The vessel in which the gold is to be cemented is described as a raw pot[5] (*una pignata rozza*), or crucible (*crogiolo*), or earthen stew-pot (*tegamento di terra*), which withstands fire, and is large enough for the purpose. An intimate mixture is made of two parts of the finely-sifted powder of old tiles or bricks, and one part of triturated common salt; and some persons add one-eighth part of green vitriol, though generally the mixture above described is sufficient. The gold is beaten out into sheets as thin as paper. The vessel is filled in the following manner:—At the bottom is put a level layer of the mixture, and upon this are placed pieces of the gold, which have been previously dipped in vinegar or a solution of sal-ammoniac in urine; then upon the gold a second layer of the mixture is spread, and so in succession, alternate layers of mixture and gold, [ending with the mixture ?] until the vessel is filled, or until all the gold to be cemented is thus interstratified with the mixture; after which the vessel is covered with an unbaked or baked tile (*tegola cruda o cotta*), luted, coated all over externally with "lutum sapientiæ," and dried. The vessel is placed on the iron bars above the grate, and the mouth or top of the furnace is covered with a tile or bricks and luted up, leaving only two or three vents at the corners for the escape of the smoke and flame. A wood-fire is made on the grate, which is gentle at first and gradually increased to such a degree as to keep the vessel red-hot, but not beyond so as to cause the gold and the cementing mixture to melt together, for in that case the mixture would cease to act. The heating is continued for 24 hours, after which the fire is lowered, or rather withdrawn, and the vessel, while still red-hot, is taken out of the furnace with tongs. The cover is removed, and the whole contents of the vessel are put into urine or common fresh water. The gold is freed from adherent powder with a bristle brush, washed by hand, and then tested as to its fineness on the touchstone. If it should not be as fine as desired, it must be re-cemented once or twice with fresh mixture; and when it is found to be sufficiently fine, it is melted with a little borax, crude soda, lime, or wood-ashes, and cast into bars or into any other forms. "And thus," writes Biringuccio, "you will have brought your gold to its ultimate perfection and fineness, and to that beautiful colour which you will see, and it will be of the same value, though its weight be diminished by that of the silver, or copper, or other thing with which it was previously associated. Nor

[4] For measuring silk, the Venetian braccia of 1540 = 2·015 English feet. I am indebted to Mr. Bullen, of the British Museum, for this information; but what was the exact length of the braccia of Biringuccio I am unable to state.

[5] Red or raw pot.

is the silver lost, as it remains absorbed in the powders: to extract it, the washings and other refuse are mixed together, made into a sort of cakes, and smelted in the blast-furnace, along with the test-bottom and other sweepings, as I have shown in the place where the smelting of litharge is described; and so all the silver, or a little less, is recovered, which was in the gold you cemented."

The following statement concerning the composition of "lutum sapientiæ" is given on the back of folio 64 of Biringuccio's treatise. "It is made of a lean earth mixed with the fourth part of all or more of the shearings of woollen cloth (*i.e.* shoddy), and about an eighth part of washed wood-ashes and the fourth part of the dung of the ass or horse or other animal, which is dry; and these things are well incorporated together and beaten with an iron rod." By "lean earth" is meant a clayey earth, which does not contract and crack too much on drying.

Agricola gives a description of this process, which is very similar to that of Biringuccio, and which is illustrated with a woodcut, showing the construction of the furnace, the form of the pots, and the mode of closing the top of the furnace, which is done by placing over it a latticed grating of iron and laying bricks or tiles thereon.[6] The ingredients of the cementing compound are, he says, to be separately pounded and sifted, and then mixed together, and the mixture is to be moistened with vinegar or the urine of man, in which a little sal-ammoniac is dissolved, if that substance be not one of the ingredients of the compound. He then states as follows:—"Quidam tamen aureos globulos aut bracteolas eadem madefacere malunt: tum alternatim in ollis novis et puris in quas nulla unquam aqua infusa fuit, collocari debent." [But some prefer to moisten the golden globules or thin plates (literally, leaves) with the same (urinous solution); then they (*i.e.* the compound and the gold) ought to be arranged alternately in new and clean pots into which no water has ever been poured.] It will thus be perceived that the gold was not always used in the form of thin plates: by the term "aureos globulos" is doubtless meant granulated gold. After stating the composition of various cementing mixtures, he expresses the following opinion respecting them:—"Quamobrem quidam nunquam talibus compositionibus, in quibus ista sunt, utuntur: et recte sane: nam solus pulvis latericius et sal, maxime fossilis, totum argentum et æs ex auro elicere et in se trahere possunt." [Wherefore some never use such compounds, in which those things are (alluding, by way of example, to verdigris and "atramentum sutorium," literally "shoemaker's black," but here meaning green vitriol or ferrous sulphate, used for colouring leather black): and very properly: for brick-powder alone and salt, especially fossil salt (rock-salt), are able to extract all the silver and copper from gold, and absorb them.]

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[6] De Re Metallicâ, 1561. lib. x. pp. 364–367. An engraving on wood of the furnace is also given by Ercker in his "Aula Subterranea."

Description of the Process of Cementation with Chloride of Sodium as practised in South America in this Century.

The best modern description of this ancient process of "dry parting" which I have met with is that of Boussingault, published in 1833;[1] and it is particularly interesting and valuable, because it is founded on his own observation. When he visited South America, it was in operation at many works, including even the mint of Bogotà (formerly Santa Fé de Bogotà), the capital of New Granada. At this mint it was always practised when native gold from the mines was received, which contained more silver than the proportion of alloy permitted by law in the coined gold; and it was there that Boussingault witnessed the following method of procedure.

The argentiferous gold is granulated, and then subjected to cementation in pots of porous earthenware. The cement is a mixture of 2 parts of brick-dust and 1 of common salt. The vessel is filled with alternate layers of cement-powder, of about an inch in thickness, and granulated gold, beginning and ending with the former. A pot may contain from 10 to 15 lbs. of gold.

The furnace is a hollow cylindrical shaft, 4½ feet in internal diameter, and 9 feet high; and at the height of 3 feet from the ground there is a grate for the pots to stand upon. At the bottom of the furnace, and level with the ground, there is an opening for charging the fuel, which is wood; but there is neither fire-grate nor chimney, the pots being put in and taken out at the top. The pots are kept at a cherry-red heat. Cementation lasts from 24 to 36 hours, according to the quantity of silver to be extracted. After the completion of the process, the contents of the pots are stirred up and washed with water, whereby the cement-powder is separated from the granulated gold; the cement-powder, after settling from the water, is reserved for further treatment, and the gold, which is usually from 21 to 22 carats fine (*i.e.* it contains from 3 to 2 parts by weight of alloy in 24 parts) is cast into bars suitable for rolling. The cement-powder is ground into a fine paste, which is mixed with $\frac{1}{10}$th of its weight of common salt, and then amalgamated with about 10 times its own weight of mercury. This operation, which lasts from 4 to 5 days, is effected in large wooden vats, at a temperature ranging from 14° C. to 18° C. This amalgam is always very "dry," owing to the large quantity of mercurous chloride with which it is intermixed. The silver from the amalgam is nearly pure, containing only a few thousandths of gold.

Boussingault proposed to apply this process to the desilverization of gold in a fine state of division, such as was procured by the washing of a certain pyrites,[2] and which usually contained 26 per cent. of silver; but before doing so, he made preliminary experiments on a small scale. He heated the mixture of the gold-powder and cement

[1] Annales de Chimie et de Physique, 1833. 54. pp. 253–263.
[2] Pyrite de marmeto.

in a Cornish crucible during 30 hours, and at a temperature, it is presumed, approximating as far as practicable to that which he saw used in the process above described; but to his surprise the standard of the gold remained the same. He repeated the experiment, prolonging it to 72 hours, and yet the gold contained almost as much silver as it did at first. In short, every experiment of the kind which he made with good crucibles (*bons creusets*) always failed; and, to the great satisfaction of the workmen, he was compelled to return to the old method.

It now struck Boussingault that, whereas in the old method imperfectly-fired and *porous* earthenware pots are used, in his experiments he had used comparatively *impermeable* crucibles, so that atmospheric air might be essential to the process, as it would easily pass into the interior of the porous pots, but not into the interior of his crucibles. In order to settle this question, he made the following experiments. A thin piece of silver, weighing 24·6 grains, was placed in the centre of a little porcelain vessel, filled with a cement made of pounded brick and common salt; and the vessel was put into a crucible lined with charcoal and covered with charcoal-powder well stamped down, every precaution being thus taken to prevent access of atmospheric air, or rather of *free* atmospheric oxygen. Another similar piece of silver was, on the contrary, placed in the cement-powder on a cupel. The first crucible was heated in an ordinary furnace, it is presumed, and the second during 7 hours in a muffle. After the experiment, the silver in the former weighed 24·3 grains, and that in the latter only 9·5 grains; the surface of this silver was strongly corroded, and the cement-powder impregnated with chloride of silver. (See pp. 69, 70 antea.)

That atmospheric air, in some way, determined the action in the last experiment, there could be little doubt; but in what manner was ascertained from the following experiments:—A piece of silver was placed on a cupel and covered with common salt, and the cupel was kept heated to redness in a muffle during 3 hours; and it was found that the silver had undergone no change. Hence it was inferred that the presence of an earth is necessary to enable common salt to change metallic silver into chloride; and as the cement-powder consists partly of clay, and as clay is composed of silica and alumina, he proceeded to ascertain what effect each of those substances separately might produce. Accordingly, two pieces of silver, each weighing 6·5 grains, were placed in two cupels respectively, one containing a mixture of silica and common salt, and the other, a mixture of alumina and common salt. The cupels were heated during 4 hours at a temperature above cherry-redness. The results were as follow:—The silver which had been in the silica mixture weighed 4 grains, and its surface presented throughout a very remarkable crystalline structure; in some spots there was an olive-green coating, which adhered strongly to the metal; those parts of the cement-powder which had been in contact with the silver were coloured deep-brown; the cement-powder had not the slightest saline taste, and was nearly

wholly vitrified; and to the latter circumstance was attributed the failure of the cementation in this instance. The silver which had been placed in the alumina mixture had completely disappeared; the cement-powder, when cold, was found to be feebly agglutinated, crystalline in structure, and brilliantly white (*sa blancheur était éclatante*), but not sensibly salt to the taste: on exposure to solar light it soon acquired a pretty deep violet tint.

Silica does not act upon common salt at a high temperature, provided both substances be perfectly dry; but, as is well known, when the vapour of water is present, most energetic action occurs, hydrochloric acid gas being evolved and silicate of soda formed. As, however, in the preceding experiment with silica, vitrification of the cement-powder had taken place, it was inferred that this action was due to the moisture in the atmospheric air which passed through the muffle. Now, in the cementation on the large scale at the Bogotá mint, vapour of water must find its way into the interior of the pots, owing to their porosity; and as they are heated with wood, they must be freely exposed to such vapour, because wood, on combustion, evolves water in large quantity.

In order more conclusively to prove this action of the vapour of water, a piece of silver was placed in a porcelain tube and surrounded with the usual cement-powder; the tube was then heated, and after it had become red-hot, a continuous current of well-dried atmospheric air was passed through it; but the silver suffered no change.

Boussingault next passed perfectly dry hydrochloric acid gas over silver heated in porcelain tubes. As soon as the metal had become red-hot, the evolution of hydrogen began, but soon ceased. On examining the silver after the experiment, its surface was found to be coated with a "varnish" of chloride of silver, to which he attributed the speedy cessation of the action. In order to test the correctness of this inference he repeated the experiment, surrounding the silver with alumina, with a view to its absorbing the chloride of silver as fast as it was formed, and while in a molten state; and the result was that the evolution of hydrogen was much more copious than in the first instance, but it gradually diminished and at last ceased entirely. The silver was strongly attacked, though still coated over with chloride of silver, which had penetrated only a very little way into the alumina. The same experiment was again repeated, but this time with the addition of common salt to the alumina, and now the action proceeded without interruption. Boussingault suggests that the chloride of sodium may favour the diffusion of the chloride of silver through the alumina, from its tendency to combine with that chloride and form a double salt. That the chloride of silver *dissolves* in molten chloride of sodium may be granted (see pp. 62, 63 of this volume), and this, I think, would suffice to explain its action in the last experiment.

In all the foregoing experiments the hydrogen was associated with a large excess of hydrochloric acid gas, and was evolved in very small bubbles. It is by reason of such excess that the formation of

chloride of silver is possible; for hydrogen easily reduces that chloride at a red-heat, and therefore requires to be swept away the instant after it is produced.

The experiment with a cement-powder consisting of alumina and common salt deserves special attention; for it seems to indicate that at a red-heat alumina, like silica, decomposes chloride of sodium in the presence of the vapour of water, with the formation of an aluminate of soda.

D'Elhuyar's Experiments bearing upon the Cementation of Silver with Chloride of Sodium.

It is not, I think, generally known to chemists that, in the last century, Don Fausto d'Elhuyar, the joint discoverer with his brother of tungsten, investigated the action of common salt on gold and silver, and by very precise experiments obtained results of much interest and importance with reference to the metallurgy of those metals. His experiments are recorded in a memoir on the theory of amalgamation, which was published in 1790,[9] and from which the following extracts have been made.

"I took," writes D'Elhuyar, "beaten-out silver leaves, and triturated them in a glass mortar with finely-powdered quartz. This quartz was originally very pure, but in order to free it completely from any particles of foreign matter, which it might have acquired during its pulverization, I digested it repeatedly with hydrochloric acid, washed it afterwards several times with distilled water, and calcined it at a very high temperature: after this treatment it had a beautiful white colour. To the mixture of silver and quartz I added some common salt, and calcined it in the muffle of an assay-furnace. During this operation, fumes of hydrochloric acid were given off, which could be seen as well as smelt. In order to extract from the calcined mixture the alkali and any of the common salt left undecomposed, it was repeatedly washed with distilled water, and the residue was digested with nitric acid. The decanted liquid was tested by the addition of a few drops of hydrochloric acid, but there was no change in the colour, nor the slightest indication of silver. The residue was again washed with distilled water, and afterwards digested with strong hydrochloric acid. As the liquid was clear, it was poured off and a portion of it diluted with distilled water, when it instantly became milky; and a precipitate was formed which in a short time acquired a pearl-grey colour, and which was nothing else than horn-silver. This experiment showed me conclusively that the vapour of hydrochloric acid powerfully attacks and dissolves silver."

"I next proceeded to ascertain whether liquid hydrochloric acid would not act in a similar manner on silver in an extremely fine state

[9] Bergbaukunde. Leipzeig bey Georg Joachim Goeschen, 1790. 2 vols. 4to, 2. pp. 200 et seq.

of division.[1] Accordingly, I triturated silver leaves with quartz, and boiled the mixture in concentrated hydrochloric acid for half an hour. On diluting with distilled water the clear supernatant liquid, after decantation, horn-silver was immediately formed. This result led me to further researches on the action of hydrochloric acid on silver in the cold. I laid a little silver leaf in a glass, and poured thereon concentrated hydrochloric acid; during the first hour I did not observe the slightest change, but afterwards the silver began to blacken, and on the following day was wholly dissolved. On diluting the solution with distilled water, horn-silver was precipitated. . . . . I took silver which had been precipitated from a solution of nitrate of silver by sheet copper, and afterwards repeatedly boiled with distilled water, and digested it in the cold in concentrated hydrochloric acid. The silver, which was in the state of very fine powder, with the exception of a few larger intermixed particles, became clotted instantaneously, as I poured the hydrochloric acid upon it. The little clots became continually smaller, and after the lapse of two days had completely disappeared. The liquid was now very clear, but instantly became milky when diluted with water, and let fall a deposit which had all the properties of horn-silver. . . . If the hydrochloric acid be very diluted, it exerts no action on silver, at least not in 24 hours. The solution is clear, and has the ordinary colour of hydrochloric acid; and the metallic salt which it contains is only kept in solution by the excess of acid; and since it is not soluble in water, at least not perceptibly so, it is precipitated when the solution is diluted. If the acid be concentrated, groups of small shining octahedral crystals are deposited in the cold. So long as the crystals remain in the acid they are white; but after the acid is poured off, they acquire, on drying, a pearl-grey colour, which subsequently passes into violet, and at last into a smoky grey. These crystals retain their lustre, do not disintegrate, and do not attract moisture from the air. When a piece of sheet-copper is dipped into the solution, it becomes instantly silvered, notwithstanding the large excess of acid. . . . With regard to solubility, all that I can state is that silver is far less soluble in hydrochloric acid than in nitric."

D'Elhuyar made other experiments which have a more direct bearing on the cementation process than those last recorded. He calcined a mixture of common salt and Carrara marble, and another of salt and porcelain clay; and in both cases there was a copious disengagement of the fumes of hydrochloric acid, only in the latter case a higher temperature was required. Mixtures of salt and gypsum (sulphate of lime) and salt and sulphate of baryta behaved in like manner; but a lower temperature than that required in the preceding experiments sufficed, particularly in the case of gypsum; and this circumstance suggested to D'Elhuyar that the sulphuric acid

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[1] As I was not aware of these experiments when I wrote the earlier part of the volume, and as no better opportunity will occur, I insert a report of them in this place, though at the risk of being charged with digressioth.

in those two salts might have caused the evolution of hydrochloric acid. A mixture of red hæmatite and common salt was also calcined, when acid fumes were evolved; but contrary to his anticipation a higher temperature was needed than in any of the foregoing experiments. If the temperature needed to cause such evolution had been the same in the first three experiments of the kind above reported, it might, he thinks, be inferred that this reaction was due to heat alone. But with quartz a lower temperature sufficed for the reaction than with marble, and with marble a lower temperature than with porcelain clay. That these substances act in a very sensible degree upon common salt is unmistakable. From a consideration of the results of his experiments, D'Elhuyar draws the following conclusions:—That the common salt was decomposed, at least in the first three experiments, in a similar manner to saltpetre; namely, by the action of those earths (so-called, silica, marble, and porcelain clay) upon the alkali of the common salt in such a way as to weaken its affinity for the acid (hydrochloric), so that the latter may be completely separated by heat and volatilized. And in further support of this view he adduces the following experiment:—He kept common salt melted in a crucible in a muffle during an hour, and found that after this treatment a solution of the salt in distilled water instantly reddened blue "sugar-paper," whence he inferred that it contained free acid; that that portion of the salt which had been in contact with the crucible had been decomposed by the clay of which the crucible was made; and that some of the acid set free had remained in the residual salt, or attached to the sides of the crucible which had been coated with clay. "Since," he adds, "it cannot be assumed that any of the alkali should have been converted into vapour and volatilized, it is not possible to account for the excess of acid in the product, otherwise than by supposing that the alkali separated had combined with another substance, which could be nothing else than the substance of the crucible."

As some of D'Elhuyar's statements appeared to me novel, interesting, and difficult to explain, I determined to test the accuracy in the Laboratory of the Royal School of Mines; and, accordingly, the following experiments were made, the results of which have in the main confirmed those statements.

Silver-leaf, quite free from copper, was boiled with hydrochloric acid of sp. gr. 1·167, when it was wholly dissolved in the course of 3 or 4 minutes.

Silver-leaf was spread over the bottom of a beaker, nearly covered with the same kind of hydrochloric acid, and left for 24 hours, when it was found to have been almost entirely dissolved: no heat was applied in this experiment.

It is probable that atmospheric oxygen tends to promote the solution of silver in hydrochloric acid—if, indeed, it be not essential to it—by forming water with the hydrogen of the acid.

Chloride of sodium in the state of common salt was kept melted, at a comparatively high temperature for about an hour, in a covered

fine-grained crucible made of French clay, heated in an air-furnace, and the vapour, which was copiously evolved, and frequently tested with moistened litmus-paper, was found to have a strongly acid reaction; and it had an odour decidedly different from that of the pure vapour of chloride of sodium. After cooling, there remained in the crucible a considerable mass of salt, which was highly crystalline and grey-coloured; and this mass throughout showed an acid reaction with litmus-paper, which was feeble in the central portion, but stronger at the exterior: it contained a little ferric and ferrous chloride, chiefly the latter, which satisfactorily accounts for its acid reaction. This and the following experiments were made with the greatest care by my assistant R. Smith, and I myself examined the products.

Common salt was heated in the same manner as in the last experiment, until the whole of it was volatilized. The outer surface of the crucible was coated with numerous patches of a brownish-red substance, which partially dissolved in water, and formed a yellow liquid, having a strongly acid reaction, and containing ferric chloride. This salt of iron appears to have resulted from the action of hydrochloric acid vapour upon the oxide of iron in the substance of the crucible; and such acid vapour, it need hardly be stated, must have been produced by the action of the silica of the crucible upon the common salt in the presence of atmospheric air, which always contains aqueous vapour.

A mixture of 50 grains of rock-salt (which was proved to be nearly chemically pure chloride of sodium), and 150 grains of sulphate of lime in the state of gypsum, both in fine powder, was exposed to a strong red-heat for about half an hour, in a shallow clay roasting dish, previously coated with powdered gypsum to the thickness of $\frac{1}{8}$ inch. At first the mixture became fissured, owing, it was presumed, to the escape of water from the gypsum, and afterwards vapour was given off, which had a strongly acid reaction, as proved by its effect at repeated intervals upon moistened litmus-paper. The odour of this vapour was different from that of the pure vapour of common salt. The substance which remained in the roasting dish was semi-fused and crystalline, and showed an alkaline reaction with litmus-paper. It was a question whether these results were not due to the action of the salt upon the substance of the roasting dish, and the consequent production of hydrochloric acid vapour and silicate of soda, the former accounting for the acid and the latter for the alkaline reaction.

In order to settle that question precisely, the same experiment was repeated in a platinum vessel coated with powdered gypsum. The mixture melted, and vapour was given off which reddened litmus-paper; and this acid reaction became more decided as the temperature increased. Some of the vapour was collected on a moistened watch-glass and tested for sulphuric acid, but not a trace of that acid was detected. The residual product was crystalline, and showed an alkaline reaction with litmus-paper. The upper part of the product where it was in contact with the platinum vessel had a yellow tint,

which was found to be due to peroxide, and not to chloride, of iron. The platinum was not in the least degree acted upon. These results may be explained by the formation of a little chloride of calcium, and its subsequent partial decomposition with the separation of lime.

A mixture of 50 grains of rock-salt and 150 grains of Carrara marble was treated in the same manner as in the experiment with gypsum, in a roasting dish coated with powdered marble to the thickness of $\frac{1}{8}$ inch. Vapour was given off, which towards the end of the experiment showed a feebly acid reaction with litmus-paper. The substance which remained in the roasting dish was slightly fritted.

This experiment was repeated, with the substitution of precipitated carbonate of lime for Carrara marble; and the result was the same as in the experiment with that substance. The odour of the vapour was different from that of the pure vapour of common salt. The roasting dish was acted on, and stained red where it had been in contact with the mixture.

The experiment was again repeated, but in a vessel of platinum instead of a roasting dish. The vapour evolved was tested several times and found to have no action on litmus-paper; and its odour was like that of the pure vapour of common salt.

Hence, it is clear that in the two experiments preceding the substance of the roasting dish was concerned in the production of the acid reaction of the vapour in those experiments.

While the production of chloride of silver in the process of cementation may be explained by the action of hydrochloric acid gas, evolved in the manner described, yet it is possible that some chlorine may also be evolved; for Oxland many years ago patented a method of producing chlorine by passing a mixture of air and hydrochloric acid over red-hot bricks;[2] and chlorine is also evolved when a mixture of silica and a chloride of an alkali-metal, alkaline earth metal, or earth-metal is heated to redness in a current of atmospheric air or oxygen.[3]

Antiquity of the Process of Cementation.

The following passage occurs in Pliny:—"Torretur [aurum] cum salis gemino pondere, triplici miseos, ac rursus cum duabus salis portionibus et una lapidis quem schiston vocant; ita virus trahit rebus una crematis in fictili vase ipsum purum et incorruptum, relicus cinis servatus in fictili olla ex aqua inlitus lichenas in facie."[4] [It (the gold) is heated with twice its weight of salt and thrice its weight of *misy*, and again with two portions of salt and one of the stone called schist; and so when these substances are burnt together in an earthen crucible, it throws out the *virus*, remaining itself pure and unadulterated; the ash which is left, being preserved in an

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[2] The title of the patent is "Improvements in the Manufacture of Chlorine." A.D. 1845, Feb. 20th, No. 10528.

[3] De Lalande and Prudhomme. Watts' Dictionary of Chemistry, 2nd Supplement, 1875. p. 321.

[4] Naturalis Historiæ lib. xxxiii. cap. iv. sect. 25. Sillig's edition. 1851. 5. p. 95.

earthen pot and applied in admixture with water as an ointment to *lichen* on the face.][5]

That the process of purifying gold by cementation with common salt is indicated in the foregoing passage, no reasonable doubt can, I think, be entertained. It may be inferred that the primary object of the process was the refining of impure gold; for Pliny states in his description of *misy* that this substance was used for purifying gold: thus, "Hoc [misy] admiscent qui aurum purgant."[6] [In purifying gold they mix it with this substance.] *Misy* is native yellow copperas, which is a basic sulphate of peroxide of iron produced by the oxidizing action of atmospheric air, or, as it is termed, weathering action, on iron-pyrites. According to Dana, it is the species of native copperas named Copiapite. Pliny records that in his day the best *misy* came from the manufactories of Cyprus. At a red-heat, and certainly far below the melting-point of gold, *misy* is resolved into sulphuric acid, which volatilizes, and into peroxide of iron, which remains; and it might, therefore, be substituted for green copperas or ferrous sulphate, which, as previously stated, appears, in conjunction with common salt, as an ingredient of some of the mixtures prescribed by the old metallurgists in the process of separating silver from argentiferous gold by cementation.

As the word "sal" is mentioned by Pliny without any remarks by way of definition, it may be concluded that common salt or chloride of sodium is meant.

The word "schistos," it is expressly stated, was applied to a stone, and the etymology of the word indicates precisely what is now understood by the expression schistose structure;[7] and it may reasonably be presumed that this stone consisted mainly of silica and alumina, and therefore might be substituted for the pounded brick in a cementing mixture.

Hence all the ingredients specified by Pliny are such as are known to have been used in later periods in the process of purifying gold by cementation. His description, also, of the manner of using them, though not detailed, and of the kind of vessel required for the purpose, is applicable to that process. There seem to have been two operations, the first in which the cementing mixture consisted of salt and *misy*, and the second in which it consisted of salt and schist.

The "virus" thrown out from the gold and retained in the residue of the cementing mixture must certainly have been some metallic impurity in the gold; but whether it was silver or some other metal, or both, can only be a matter of conjecture. As the "ash" or residue of the cementing mixture was used as a remedy for a cutaneous disease of the face named "lichen," the question arises,

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[5] I am indebted to my friend Mr. Philip Smith for an elaborate critical analysis of the foregoing passage, and for the translation of it here presented. With reference to its grammatical construction there are points of difficulty.

[6] Lib. xxxiv. cap. xii. sect. 31. Sillig's edition, 5. p. 176.

[7] Schistos, a, on, *adj.*=σχιστός, *split, cleft, divided.* A Latin-English Dictionary. By William Smith, D.C.L., LL.D. 1872.

what was the remedial agent in the "ash"? Was it chloride of silver, or a compound containing another metal derived from the gold, or some of the *misy* left undecomposed? To this question no satisfactory answer can now be given. *Misy*, it may be stated, is mentioned by Paulus Ægineta as one of the remedies for "lichen";[8] but if that had been the only agent, it seems to have been hardly worth the trouble of preserving the "ash" as a substitute for *misy* in its natural state.

Rossignol, in an article on the "Electrum" of the ancients, cites a passage from Strabo, which indicates the separation of silver from an alloy of gold and silver either by a process of cementation, or by fusion, but without the use of common salt.[9] "Ici se présente la question, si les anciens savaient faire le départ ou la séparation de l'or et de l'argent, sans perdre du moins ce dernier métal. Un juge très-expert dans la matière, Savot, leur a dénié absolument cette connaissance, et il s'appuie de quelques Lois du *Digeste*, qui prêtent à ses paroles une grave confirmation (*Discours sur les Médailles antiques*, p. 79 sqq.).[1] Je puis fortifier son opinion d'une preuve nouvelle et plus concluante encore peut-être. Strabon parlant de l'or de l'Espagne, nous dit: 'De l'or cuit et purifié à l'aide d'une certaine terre alumineuse, il reste un résidu qui forme de l'électre; si l'on recuit ensuite ce résidu, qui contient de l'argent et de l'or, l'argent se consume et l'or reste au fond.'—'Εκ δὲ τοῦ χρυσοῦ ἑψομένου καὶ καθαιρομένου στυπτηρώδει τινὶ γῇ τὸ κάθαρμα ἤλεκτρον εἶναι· πάλιν δὲ τούτου καθεψομένου, μίγμα ἔχοντος ἀργύρου καὶ χρυσοῦ, τὸν μὲν ἄργυρον ἀποκαίεσθαι, τὸν δὲ χρυσὸν ὑπομένειν (Lib. iii. p. 146, edit. Casaub.). Quoiqu'il ne soit point dit ce qu'est devenu l'argent dans la première opération, on présume sans peine qu'il a subi le même sort que dans la seconde, qu'*il s'est consumé*." For the following translation of the above passage, which differs from that of Rossignol, I am indebted to my friend Dr. William Smith:—"If the gold is heated and purified by a kind of earth called stypteria, what is thrown off in purification is electrum. But if this, which contains a mixture of silver and gold, is again heated, the silver is burnt away, but the gold remains."

The gold mentioned by Strabo was the native metal found in Andalusia in the South of Spain, where it was obtained not only by washing the sand brought down by rivers and torrents, but also by actual mining. All native gold, without any exception so far as I know, contains silver, the proportion of which varies greatly in gold

[8] The seven Books of Paulus Ægineta. Translated from the Greek by Francis Adams. Published by the Sydenham Society. 1846. 2. p. 24.

[9] Les Métaux dans l'Antiquite. Par J. P. Rossignol, Membre de l'Institut, Professeur de Littérature Grecque au Collége de France. Paris, 1863. p. 366.

[1] In Savot's essay entitled "Recherches sur la Métallurgie des Anciens," published in Gobet's volume, entitled "Les Anciens Minéralogistes du Royaume de France," Paris, 1779, I do not find that Savot has expressed such a positive opinion as Rossignol mentions. What he does state is, that the ancients were ignorant of the method of parting by nitric acid. Thus he writes, "C'est chose toute asseurée que l'art de separer l'or d'avec l'argent, par le moyen de l'eau forte, n'a pas esté cogneu des Anciens, à cause que l'eau forte *est d'invention moderne*" (p. 847).

from different localities, and in some cases exceeds that which existed in any of the alloys designated electrum. "Electrum" is a pale yellow or amber-coloured alloy of gold and silver to which both the Greeks and Romans gave that name.[2] There was natural electrum as well as artificial electrum; and the latter, according to Pliny, contained 20% of silver.[3] Golden foil taken by Schliemann from a tomb at Mycenæ has been recently analysed by my assistant R. Smith in the metallurgical laboratory of the Royal School of Mines, and found to have the following composition per cent.:—

Gold	73·11
Silver	23·37
Copper	2·22
Lead	0·35
Iron	0·24
	99·29

Hence it may be inferred that the metal of which this foil consisted would have been termed electrum by the Greeks. An alloy of 75% of gold and 25% of silver has a decided gold-yellow colour; but when the silver amounts to 33·3% the alloy is much paler in colour, and alloys containing more than about that proportion of silver have no golden tint.

With reference to the interpretation of Strabo's description, the question arises, what is meant by the expression which Rossignol translates "aluminous earth"? It is true that the word "στυπτηρία" is usually translated "alum," and is the source of the English word styptic, which means a property eminently characteristic of that substance. Beckmann, however, maintained that the alum of the ancients was green vitriol or ferrous sulphate, and not any of the compounds of alumina to which the word alum is now applied.[4] Adams, on the contrary, in his commentary on Paulus Ægineta, dissents from this conclusion of Beckmann on the following grounds:—"The ancients, indeed, may not always distinguish accurately the latter from the 'sulphate of alum [*sic*, but it should be alumina] and potash,' but considering how common this mineral is in the countries bordering upon the Mediterranean, we cannot conceive how the ancients could possibly have remained ignorant of it, and we need scarcely add that it has never been described by them under any other name."[5] Although alum is not so common in those localities as Adams asserts, yet Beckmann's conclusion may be reasonably doubted. But this is a subject which cannot be fully examined in this volume.

That the "στυπτηρία" of the Greeks, or the "alumen" of the

[2] The same name was applied to amber, which Rossignol asserts, on what seems to be conclusive evidence, was not known to the ancients until long after the alloy called "electrum" had been in use. (See op. cit. p. 347.)

[3] Naturalis Historiæ, lib. xxxiii. c. 23.

[4] A History of Inventions and Discoveries. Translated from the German by William Johnston. London, 1814. 2nd ed. 1. p. 288.

[5] Op. cit. p. 360.

Romans, signified either native green vitriol or native alum, or both, here can be little doubt. Now, as either of those substances, when heated sufficiently, evolves sulphuric acid, either might produce the effect which appears to be indicated in the passage from Strabo. If it be assumed that the subject of treatment was a native alloy of gold and silver, which contained so much of the latter metal as to have rendered it whiter than electrum, then by heating and reheating it with green vitriol or alum, under suitable conditions of temperature, silver would be removed in sensible quantity, and "electrum" of the characteristic colour might consequently be obtained. But it may be urged that it is not probable that Strabo would have applied the word gold to an alloy of gold and silver containing more silver than "electrum;" and this objection, which Mr. Gladstone mentioned to me, has considerable force. There is also another objection to the interpretation which I have suggested; namely, that, according to the translation of the passage in question which I have received from Mr. Gladstone, Dr. Smith, the Rev. Mark Pattison, Rector of Lincoln College, Oxford, and the Very Rev. J. W. Blakesley, Dean of Lincoln, electrum was procured from the impurity thrown off in the process, which, if my interpretation be correct, should have contained silver but not gold. The translation, however, of this passage by Mr. E. H. Bunbury agrees with that interpretation, so far as relates to the source of the electrum, which I have ventured to suggest solely on metallurgical grounds. Mr. Bunbury, who is an accomplished Greek scholar and has made Strabo a special subject of study, has favoured me with the following critical remarks on the passage in question:—

I am confirmed in the opinion that by τὸ κάθαρμα Strabo can mean nothing else than "the purified metal;" and I am gratified to find that the German translator Groskurd, whose translation of Strabo is by far the best, indeed the only one of any value in point of scholarship, takes the same view that I do. He renders the words ἐκ δὲ τοῦ χρυσοῦ . . . . ἤλεκτρον εἶναι as follows:—"Ist das Gold geschmolzen, und durch eine gewisse vitriolische Erde gereinigt, so ist *die Reinmasse* Elektron oder Silbergold."[6] It is true that in the classical Greek writers κάθαρμα is, I believe, always used in the sense of that which is driven off by purification, scum or off-scourings—whence the familiar use of it metaphorically for a worthless fellow, a thorough villain—and would therefore naturally mean dross, or slag, rather than the pure metal: but in this passage the order of the ideas seems to me clearly to require the sense I would give it: and it is not uncommon to find in Strabo words thus used in senses different from what they bear in writers of a more classical time. I do not know, moreover, that there is any instance of the use of κάθαρμα in the precise sense of dross or slag resulting from the smelting of metals.

Hamilton, also, translates the passage in the same manner as Mr. Bunbury, thus: "And that when they have melted the gold, and purified it by means of a kind of aluminous earth, the residue left is electrum. This, which contains a mixture of silver and gold, being again subjected to the fire, the silver is separated and the gold left [pure]."[7]

[6] Strabon von Groskurd. Berlin, 1831–34. 1. p. 243.

[7] The Geography of Strabo. Literally translated, with notes. The first six books by H. C. Hamilton, Esq. The remainder by W. Falconer, M.A., late Fellow of Exeter College, Oxford. London: Henry G. Bohn. 1. p. 220.

The passage is undoubtedly obscure, and the obscurity was probably due to Strabo's imperfect knowledge of the subject; for he was a geographer, and may have been as incompetent correctly to describe a metallurgical process as many a modern professor of that popular science would be. Strabo's description, however, clearly shows that a method of separating silver from gold was known and practised in Spain in his time, and that is a fact of considerable interest in metallurgical history. But centuries before that period the ancients must have been able to effect such a separation; for otherwise it is impossible to account for the remarkable purity of the gold of many of their coins. Thus Lenormant writes, "En général, dans tout le monde hellénique, la monnaie d'or et d'argent se montre à nous avec un titre remarquablement pur. Presque partout, l'or est souvent sans alliage; l'analyse ne révèle que 3 millièmes d'argent uni à l'or dans les statères de Philippe de Macédoine et d'Alexandre; c'est le plus grand degré de pureté auquel on pût atteindre avec les procédés d'affinage dont disposaient les anciens."[8]

The Japanese practise the art of communicating the colour of gold to the surfaces of articles consisting of a white alloy of gold and silver; and, although I have no account of their method, I have little doubt that the effect is produced by a superficial separation of silver. I have in my possession one of the large oval coins, known by the name of "Obang," which has the colour of gold; it is about 5·4" long and 3·2" broad, and is stamped with the Emperor's private crest and certain mint marks. On cutting off a piece for analysis, the substance of the metal was found to be white, the surface only having the colour of gold. The metal is an alloy of 36·75 per cent. of gold and 63·25 per cent. of silver, with a little copper. On heating the cut-off piece to redness, the surface immediately lost its golden colour and became white; but the original golden colour was restored to the surface thus whitened by digestion with somewhat diluted hot sulphuric acid.

SEPARATION OF SILVER FROM MOLTEN GOLD BY CHLORINE GAS.

On November 1st, 1838, Mr. Lewis Thompson made a communication to the Society of Arts on the purification of gold by chlorine gas, for which he was presented by the Society with the sum of 20 guineas; and his paper on the subject was published in their Transactions in 1840–1,[9] from which paper the following particulars are extracted:—"The plan," writes Mr. Thompson, "which I now propose for assaying and purifying gold is no less simple in execution than certain in effect, and is founded upon a circumstance long known to chemists, viz.:—that not only has gold no affinity for chlorine at a red-heat, but that it actually parts with it at that temperature, although previously combined; that is to say, the chloride of gold

[8] La Monnaie dans l'Antiquité. Leçons professées dans la Chaire d'Archéologie en 1875-1877. Par François Lenormant. Paris, 1878. 1. p. 187.

[9] Vol. 53, part 1. p. 16.

s reduced to the metallic state by heat alone, [and] it cannot, therefore, possess any affinity for chlorine when red-hot: this, however, is not the case with those metals with which gold is usually alloyed; it offers, therefore, at once an easy and certain means of separation. The application of these facts is all, therefore, to which I can lay claim, as the facts themselves have been known for many years, and the reason why they have not been so applied is, that hitherto chemists have not directed their attention to this art, but have left it entirely in the hands of the assayers, who are, for the most part, ignorant of chemistry. The process here proposed has been abundantly tested by myself and others, and employed by those wholly unacquainted with chemistry, as well as by men eminent in that science, with equal success. There is, indeed, but one source of failure, and this arises from the intense action of chlorine upon the baser metals when melted, by which portions of the alloy are spirted up or projected from the cupel, as happens in the common mode of assaying silver when the heat is too great [see the article on Assaying in this volume: the spirting is not caused by excess of heat]. This inconvenience is to be avoided in two ways. Firstly, by allowing the chlorine to be evolved slowly at the commencement of the operation, by which the intensity of the action at first is diminished, until the relative proportion of gold in the alloy is increased; or, secondly, by passing the chlorine over the alloy in powder, or laminated into a thin plate, at a dull red-heat for a few minutes, and then raising the temperature so as to melt it when the fumes of the metallic chlorides have visibly diminished. A very little practice will enable anyone to make assays of gold with the greatest accuracy. In a course of experiments, conducted in the presence of Mr. A. Aikin [in his Laboratory at Guy's Hospital, of which he was the teacher of chemistry at the time.—J. P.], and other scientific gentlemen, a piece of gold was twice alloyed, and then purified by chlorine, without any sensible loss when weighed in a balance which readily turned with the $\frac{1}{100}$th of a grain.

"The furnace which I employ for the process is made out of one of those pots employed for melting steel, and which cost about 1*s.* 6*d.* each. They are from 14″ to 16″ in height, and consist principally of Stourbridge clay and coke. Their form is rather peculiar, as the upper part is contracted so as to form a kind of dome. One of these pots is pierced near the bottom with four holes, at equal distances from each other and from the bottom; parallel to and between them, but about 2″ higher up, another row of similar holes is placed, the whole of which holes should be from $\frac{1}{2}$″ to $\frac{3}{4}$″ in diameter; about 3″ above these the sides of the pot are perforated with two larger holes of at least 1″ in diameter. These must be diametrically opposed to each other, and upon the same level, *i.e.* at equal distances from the bottom.

"To assay gold, place an earthenware tube in the two upper holes, and light the furnace (a mixture of coke and charcoal answers best, though coke alone will do); when the tube is seen to be white-

hot, place in it the alloy contained in a little cupel made of bone-ash, and push it along to the centre of the furnace by means of a wire, then connect one end of the tube with a bottle in which chlorine is forming from a mixture of peroxide of manganese and muriatic acid; the chlorine will, consequently, pass along the heated tube and over the melted alloy, with the silver, copper, etc., of which it will combine and leave the gold pure and untouched. During the process dense fumes may be observed to fill the tube, and when these are no longer produced the process is finished; the cupel may now be withdrawn, and the gold removed and weighed."

Appended to Mr. Thompson's paper is the following report by Mr. Arthur Aikin, an able and erudite chemist of the day, author of the well-known compendious and still valuable Dictionary of Chemistry and of various papers, relating to practical chemistry and metallurgy, and secretary of the Society of Arts. As this report is interesting, important, and short, I present it *in extenso*.

"The experiments above alluded to as having been made in my laboratory, were conducted by Mr. Thompson himself under my inspection. The gold was obtained from an assayer, and was stated to be perfectly pure; but in many instances, on being subjected at a melting heat to the action of chlorine gas, a very small diminution in weight was observed, occasioned, no doubt, by the volatilization of a little alloy, for the button of gold underwent no further diminution whatever on a repetition of the process. The gold thus purified was mixed with silver and copper, or with silver and brass; and, being put into a small porcelain tray, with a little chalk or common salt, was slidden cautiously to the hottest part of the tube. When the alloy was judged to be melted, chlorine gas was passed in at one end of the tube, the other either being left quite open or communicating with a small glass retort to collect the volatile products. A dense yellowish vapour almost immediately filled the tube, part of which concreted in filamentous crystals in the end of the tube; the remainder passed into the retort, lining it with a brownish yellow crust, or, if a little water had been put into the retort, producing a greenish liquor which, by the usual tests, was shown to contain chlorides of copper, zinc, and iron. The latter was, no doubt, derived from the ferruginous clay of which the tube was made, for the inside of it, after the process, was found to be nearly white.

"On examining the contents of the tray, after the production of vapour had ceased, the button of gold was found imbedded in a melted mass of chloride of sodium (or chloride of calcium, if chalk had been put into the tray) *mixed with chloride of silver, the presence of alkaline chloride seeming to have the property of preventing the volatilization of chloride of silver.* [The italics are mine.—J. P.]

"In all the first trials, the button of gold was found to weigh considerably less than before the process, and the accidental breaking of one of the tubes showed that in the part directly over the tray several globules of gold adhered, having probably been thrown up thither by the ebullition of the alloy when the chlorine was first passed over it

Having thus discovered the cause of the failure, the process was twice more repeated, taking care to give only a low red-heat in the beginning, and to pass the chlorine slowly. With these precautions, the button of gold, remaining at the end of the process, was found to be exactly equal to its original weight, as shown by a balance that indicated well to the $\frac{1}{200}$th part of a grain."

The foregoing extracts establish the fact, that 40 years ago (*i.e.* before 1878) *gaseous* chlorine was proposed as the agent for separating from gold, while in a *molten* state, any silver, and any of the so-called "baser metals," such as copper, lead, and zinc, with which it might be alloyed; that the efficiency of this process was demonstrated experimentally not only by him who proposed it, but also by other persons, especially by Aikin, a distinguished practical chemist of the day; and further, that the process was published in the widely-circulated Transactions of the Society of Arts. Moreover, it was shown that molten gold, after purification by this treatment, suffers no sensible loss in weight by the further action of gaseous chlorine, and that while the "baser metals" are volatilized in dense fumes, chloride of silver remains with the gold, when common salt is used, "the presence of alkaline chloride seeming to have the property of preventing the volatilization of chloride of silver."[1] It may, however, be said that as, in the experiments recorded, only a small quantity of gold was operated upon, the applicability of the process on a large scale was not proved. That is certainly true; but all inventions are tried at first on a small scale; and, after the evidence which has been advanced, it cannot be denied that to Thompson is due the credit of having originated the process of separating silver and the "baser metals" from gold, while in a molten state, by the action of gaseous chlorine, unless, perchance, it should be discovered that Thompson has himself been anticipated.

In 1867, Mr. Francis Bowyer Miller, Assayer at the branch of the Royal Mint, Sydney, New South Wales, and brother of the late Dr. Miller, Professor of Chemistry at King's College, London, obtained a patent for an "Improved Method of Toughening Brittle Gold, of Refining Alloyed Gold, and of Separating therefrom any Silver they may contain,"[2] which method is precisely the same in principle as that of Thompson. The title of the patent, however, does not agree with the specification in one respect, for *two* methods are described, namely, the passing of chlorine gas, or of hydrochloric acid gas in admixture with atmospheric air or oxygen, through molten gold. The first of these methods was introduced on the large scale at the Sydney Mint, and is, I believe, the only one as yet carried into practice anywhere; and I have much pleasure in acknowledging my obligation to my friend the Deputy-Master of that mint,[3] General Ward, R.E., for supplying me with the fullest official information on the subject,

[1] See p. 69 of this volume.

[2] A.D. 1867, 17th June, No. 1767. Sealed December 10th, 1867.

[3] The Sydney Mint was regarded as a branch of the Royal Mint in London, of which at present the Master is the Chancellor of the Exchequer.

and to Mr. Miller also for various communications respecting his process. I may here express my conviction, which I have reason to know is well founded, that Mr. Miller, when he obtained his patent, had neither seen nor heard of what Thompson had published so long previously; and that he is, therefore, justly entitled to the credit of an independent inventor. But he is also entitled to the additional credit of having been the first to apply the process successfully on the large scale, especially with a view to the saving of the silver, which is a very important point; and the difficulties which have to be encountered in carrying out a novel invention on the large scale are often so formidable as to require the greatest ingenuity and perseverance in overcoming them; insomuch that, in many cases, it may be truly asserted that a far higher degree of credit is due to the man who renders an invention practicable than to him with whom it originated.

All native gold, without a single exception so far as is at present known, contains silver. In New South Wales, the gold (after melting the gold-dust) from Boonoo Boonoo, in the northern district, contains the largest proportion of silver, which ranges from 29·8% to 33·7%; while that from Nerrigundah, in the southern district, contains the smallest proportion, which is 1·5%. Gold from Victoria contains, on the average, 3·5% of silver, and 0·5% of base metals; and that from Queensland contains, on the average, 12%, that from Maryborough in the same colony containing as much as 14%. Gold from the Thames district in New Zealand, which has been coined at the Sydney Mint, approximates in composition to that from Boonoo Boonoo. Now, according to official returns, 6,820,198 ozs. of gold were received for coinage at the Sydney Mint between its establishment in May 1855 and December 31st, 1868. Hence it will be perceived that the extraction of silver from gold is a question of great pecuniary importance. But in Australia, it is alleged that the process of parting by sulphuric acid cannot be so economically practised as in Europe; and, accordingly, a large amount of silver has been there lost, by leaving it to replace copper in the coined gold, which must contain 22 parts by weight of fine gold in 24 parts, that being the legal standard of fineness. The alloy directed to be used in standard gold is copper; but it is permitted to substitute silver, wholly or in part, for this copper, a very costly substitute indeed. Australian sovereigns of former years were easily recognized by their pale tint, which was due to silver. Miller estimates that the gross amount of silver, contained in the 6,820,198 ozs. of gold above mentioned, amounted to 334,190 ozs., *i.e.* at the rate of 24,750 ozs. per annum. But at the date of Miller's paper, from which these figures are extracted, the average proportional quantity of silver contained in the gold arriving in Sydney was much greater, owing to the large amount of silvery gold at that time being found, especially in Queensland; and during the year 1868, the quantity of silver was not less than 36,000 ozs., of the value of £9150, and was probably, including that in the gold shipped direct as bullion by the banks, nearer 42,000 ozs.

Moreover, according to Miller, a very large proportion of the gold

of Australia, particularly that obtained by amalgamation from quartz veins, is more or less brittle, owing generally to the presence of small quantities of lead or antimony, which render the gold quite unfit either for coinage or manufacture. Hence it was necessary to remove those contaminating metals, which was done either by fusion with nitre and borax, oxide of copper, or corrosive sublimate. The first two of these methods are troublesome on account of the attendant corrosion of the crucibles; but the third is the most objectionable on account of the dense and highly noxious fumes which are produced. In Victoria, Miller states, these fumes were regarded as so serious a matter in a public and sanitary point of view, as to have induced the Municipal Council of Melbourne to institute an action at law against the Union Bank, which used the corrosive sublimate method at their gold-melting establishment, and compel them to abate the nuisance.

Now, by the chlorine process under consideration, two objects are effected at the same time,—namely, the separation and saving of the silver in the gold, and the removal of brittleness when brittle gold is the subject of that treatment; and to Miller is undoubtedly due the credit of having satisfactorily solved those two important problems by one and the same operation.

Miller states that it was from a consideration of the "large and costly plant," as well as the time needed for the refining of gold by sulphuric or nitric acid; the objection to the use of corrosive sublimate in the toughening of gold, both on the grounds of expense and the noxious vapours attendant on its use; and to oxide of copper or nitre and borax, on account of their corrosive action on the crucibles, with an additional objection in the case of oxide of copper,—namely, the unavoidable introduction of copper into the toughened gold,—that he was led to make experiments "for the purpose of determining whether it was not possible in one operation to satisfy all the requirements of the case more simply and cheaply." The old practice of toughening brittle gold by means of corrosive sublimate or mercuric chloride, "naturally," he says, "suggested the use of chlorine gas" as a substitute; for the active element in corrosive sublimate is its chlorine, which converts into more or less volatile chlorides the base metals in the gold, on which its brittleness depends. He then adds, "The well-known property of this gas to form argentic chloride when passed over red-hot silver, encouraged the anticipation that it might, when applied to the alloys of gold and silver, give rise to the same compound,"[4]—an anticipation, the correctness of which it hardly needed fresh experiments to confirm, after the experience of centuries in the separation of silver from gold by the process of cementation with chloride of sodium.

But Miller feared there might be great difficulty in saving the silver, owing to the volatilization of the chloride of silver and its

[4] The preceding as well as following extracts are from a paper by Miller in the Journal of the Chemical Society, London, Dec. 1868, and from another by him in the Transactions of the Royal Society of New South Wales, Dec. 1st, 1869.

absorption by the substance of the crucibles used in the process; and, accordingly, he made the following experiments.

A mixture of 922·63 grs. of chloride of silver and 1660 grs. of fused borax was put into a weighed porcelain crucible, loosely covered with a porcelain lid, and exposed during an hour and 35 minutes to the highest temperature attainable in an assay-muffle; by which treatment it was found that the crucible and its contents lost only 5½ grs. in weight.

In the next experiment a clay crucible was used, prepared in the following manner, with a view to render its substance impervious to molten chloride of silver: it was immersed in a hot saturated aqueous solution of borax, so that it might become thoroughly impregnated therewith, after which it was dried. In such a crucible, covered with a well-fitting and luted lid, chloride of silver was exposed to a high temperature in a furnace during 25 minutes; after which it was taken out, and, when cold, broken: it contained a cake of chloride of silver of nearly the same weight as the original chloride, and "no absorption of chloride by the crucible was found to have occurred."

In a third experiment, recorded by Miller, 102 ozs. of fine silver and 3 ozs. of fused borax were melted together in a clay crucible, prepared as just described, and covered with a well-fitting, but not luted lid, having a hole in the centre, through which a clay-pipe was introduced as soon as the contents of the crucible had become molten, the pipe reaching to the bottom. Through this pipe a current of chlorine gas passed for more than an hour, without any projection of globules of silver being observed. After this, the crucible was withdrawn, left to cool, and then broken, when a cake of silver was found at the bottom, covered with a layer of chloride of silver,[5] on which was a thin layer of borax of a delicate pink colour. The weight of the chloride of silver thus formed was 14·93 ozs., from which an ingot of silver, weighing 10·81 ozs., was obtained. The crucible, on being crushed and washed, yielded 0·08 oz. of silver; and the borax 0·06 oz. From these data it will be seen that the loss of silver on 102 ozs. amounted only to 0·22 oz. Miller remarks that "in these experiments the small addition of borax appears to have prevented all but a very minute volatilization of argentic chloride."

Miller seems to suppose that he was the first to discover the comparative fixedness of chloride of silver at a high temperature; for, in his paper read before the Chemical Society, he thus expressed himself: "Indeed, so much does this question (*i.e.* the volatility of chloride of silver at high temperatures) seem to involve the whole success of the application of chlorine gas to the purposes in view that there can be little doubt but *that a foregone conclusion on this point* has hitherto prevented such a process from receiving earlier attention and trial." [The italics are mine.—J. P.] But in that supposition Miller is mistaken; for, as previously stated at p. 57 of this volume, this fact was observed by Malaguti and Durocher

[5] It is hardly necessary to remind the reader, that the specific gravity of chloride of silver is much less than that of gold.

and recorded by them in these unmistakable words: "Le chlorure d'argent seul exige une température très-élevée pour se volatiliser, et en outre sa volatilisation en vase clos est très-lente à cause de la faible tension de sa vapeur."[6] Besides, as we have seen, Aikin, in his report of experiments on Thompson's process, has particularly noticed the fact of the seemingly feeble volatility of chloride of silver, at the melting-point of gold, in a current of gaseous chlorine, in the presence of chloride of sodium. (See also pp. 69 and 70 of this volume.)

The next step taken by Miller in the course of his investigation was to operate upon argentiferous gold, using for this purpose clay crucibles prepared with borax, and not plumbago crucibles, which he found would not answer, owing to their exerting a reducing action on chloride of silver, which, he thought, was probably due to a small quantity of hydrogen existing in the materials of which such crucibles are made. The crucible was covered with a closely-fitting, but unluted lid, having a hole through the middle, and the tube which he used was the stem of a long common tobacco-pipe. The upper end of this pipe was connected, by means of a vulcanized india-rubber tube, with a large stoneware bottle, containing ingredients suitable for the production of chlorine, and warmed in a water-bath. The chlorine gas was not dried, but passed into the crucible just as it issued from the generator, as he had found that nothing was gained by drying the gas. The chlorine-generator was fitted with a safety-tube 7′ long, dipping, at its lower end, into the liquid in the generator; and the height of the column of liquid in this tube being such as was necessary to overcome the pressure of the column of molten gold in the crucible, any sensible lowering of it instantly showed that an accident must have happened to the clay-pipe, that the joints of the chlorine apparatus had become leaky, or that the crucible had cracked. A column of 1″ of molten gold in the crucible was found to be equivalent to a column of from about 16″ to 18″ high in the safety-tube. The india-rubber tubing stood the heat well, when protected from the direct radiation of the fire; and, if plunged into weak ammonia-water at the end of each operation, lasted uninjured for some time. In the simple apparatus above described from 135 to 409 ozs. of gold were treated at a time; and about 8 ozs. of metallic silver per hour were separated in the state of chloride, and at a nearly uniform rate, whether the gold were alloyed with much or little silver.

No difficulty was experienced from the projection of globules of gold. Most of the chlorine seems to be absorbed at once, and, consequently, violent ebullition does not occur. It was found advisable not to pass the chlorine into the molten gold until all the atmospheric air in the generator had been expelled; because air passed through without being absorbed, and so caused rather more bubbling of the molten gold, with possible loss by projection, than was the

[6] Recherches sur l'Association de l'Argent aux Minéraux métalliques, etc., 1850. p. 315.

case with pure chlorine gas, which was almost wholly absorbed by the silver.

The progress of the operation was ascertained by assaying at intervals portions of the molten gold, obtained by dipping into it a clay-pipe, previously warmed in order to prevent its cracking, and then withdrawing the pipe, closing at the same time its upper end, as is done with a pipette. By this means, a little wire-like piece of gold was procured, which was forthwith approximately assayed.

When the operation was completed, the crucible was taken out of the furnace, and left to cool until the gold had solidified, when the chlorides on its surface, being still liquid, were poured off into a mould, so as to form them into a slab; while the borax, owing to its viscousness, remained in the crucible. The molten mass of chlorides appeared to have the property of dissolving a little chlorine gas, which escaped, with sluggish effervescence, as the mass cooled. The gold left in the crucible was re-melted and cast into ingots. The slab of chlorides[7] was placed between two flat pieces of wrought-iron, and the whole immersed in water acidulated with sulphuric acid, and there left for 24 hours, after the lapse of which the reduction of the chloride of silver was usually found to be complete; but, as the silver thus obtained always contained a little gold, it became necessary to part it with nitric acid. In subsequent experiments, however, it was found possible to obtain the chloride of silver free from gold, a matter of much importance in a practical point of view. When the spongy silver procured by reduction with iron in the manner described was dissolved in nitric acid, the gold was left in a flaky state, and not in rounded globules, as, Miller reasonably suggests, would probably have been the case, if it had been mechanically thrown up during the passing of the chlorine gas. This is an interesting observation, and, as Miller says, seems to indicate that the gold in the slab exists in the state of chloride; but he adds that, on re-melting the slab at a red-heat, part of the gold was readily separated in the metallic state, while another part still remained with the chloride of silver. Hence he inferred that, if some agent could be found which would reduce chloride of gold and not chloride of silver, the whole of the gold might be thereby obtained from the slab by simply re-melting it along with that agent; and it occurred to him that silver itself might prove to be such an agent, which turned out to be the case, as will appear from the following experiment.

A slab of chloride of silver weighing 13·22 ozs., which had been produced by the action of chlorine on molten argentiferous gold, and contained a small quantity of gold, was fused in a clay crucible, prepared with borax, and kept at a bright red-heat for 5 minutes, after which $\frac{1}{2}$ oz. of carbonate of potash was gradually "dusted" into the crucible, and the crucible left in the furnace for 20 minutes longer. By the reducing action of the carbonate of potash on a small quantity of the chloride of silver, there was produced "a shower of

[7] Probably the only chloride, besides chloride of silver, was cuprous chloride; for cupric chloride is reduced at a red-heat to cuprous chloride, with the loss of half of its chlorine.

minute globules of metallic silver," which, in descending through the molten chloride of silver, reduced any chloride of gold that might be present. After withdrawing the crucible from the furnace, and leaving it to cool until the chlorides appeared black, but were still quite liquid, they were poured off into a mould, when there remained at the bottom of the crucible a button of silvery gold, together with a spongy mass apparently consisting of subchloride of silver (argentous chloride), less fusible than the chloride. The crucible was replaced in the furnace along with the silvery button and the spongy residue; and a little carbonate of soda being added with a view to reduce any chloride of silver, etc., the whole was raised to a bright red-heat and kept at that temperature for 5 minutes. By this means a button of silvery gold was produced, which weighed 0·55 oz. and contained 0·28 oz. of gold and 0·27 oz. of silver. On reducing the slab of chloride of silver to the metallic state, and dissolving the resulting silver in nitric acid, it was found to be *quite free from gold.*

In the preceding experiments it was ascertained that about as much chlorine escaped uncombined from the argentiferous molten gold as would theoretically have sufficed to convert the whole of the silver which it contained into chloride.

The numerical results obtained in those experiments are recorded in the table subjoined:—

TABLE SHOWING THE RESULTS OF THE EXPERIMENTS OF MR. MILLER IN REFINING GOLD BY CHLORINE GAS.

Number of the experiment.	Gross weight of argentiferous gold operated upon,	Containing according to assay,		Weight of silver extracted.	Weight of alloy left after the operation,	Containing according to assay,		Apparent loss in operating.		Assay of alloy operated upon.	Assay of refined gold.
		Gold.	Silver.			Gold.	Silver.	Gold.	Silver.		
	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.		
I.	135·350	129·850	5·440	4·700	130·460	129·840	0·620	0·010	0·120	959·4	995·2
II.	194·925	166·076	28·300	27·173	166·801	165·966	0·835	0·110	0·292	852·0	995·0
III.	276·499	255·165	20·765	18·135	256·820	255·080	1·800	0·085	0·830	922·8	993·0
IV.	377·960	336·309	39·651	32·950	341·090	336·212	4·874	0·093	1·827	889·8	987·9
V.	409 250	375·280	32·740	29·606	377·050	375·111	1·939	0·169	1·201	917·0	995·0
VI.	229·800	212·100	17·510	15·580	213·620	212·090	1·530	0·010	0·400	923·0	993·0
	Before refining.				After refining.						

NOTE.—By "apparent loss" is meant the loss shown at the end of each experiment, without taking into account the amount recoverable from "sweep" and flues, which is a considerable proportion of the whole loss. [A few errors in some of the decimals have been detected, but I leave the table as Miller published it.—J. P.].

Miller has not published, so far as I am aware, the results of any experiments on the second method of desilverizing molten gold described in the specification of his patent, namely, by the joint action of hydrochloric acid and oxygen or atmospheric air; and it is therefore reasonable to suppose that he has either not made such experiments, or that, having made them, he failed to effect his object in a satisfactory manner; in which case it would have been safer not to have included this second method in his specification. The cooling effect of a mixed current of hydrochloric acid and oxygen or atmospheric air might, I imagine, render this impracticable.

APPARATUS AND MODE OF CONDUCTING THE PROCESS OF REFINING GOLD BY CHLORINE ON THE LARGE SCALE.

FURNACE.—The furnace is 12″ square, such as is commonly used for gold-melting. The flue should be as near the top as possible, so that the crucible may stand high up in the furnace without being cooled by the draught; and the depth of the furnace should be such that the bottom of the crucible may not be more than 3″ above the fire-bars. The mouth of the furnace is closed with two fire-tiles, each $7\frac{1}{2}$″ wide and 15″ long, and one of which has a hole or long slot in its centre. An iron cover does not answer, as it becomes too hot for convenient working.

CRUCIBLES.—Clay crucibles are used, suitable for the refining of from 600 to 700 ozs. of gold in each, and those recommended are the "Creusets de Paris," manufactured by De Ruelle, late Payen, Rue Pierre Levée, Paris, and distinguished by the numbers 17 and 18. [But I am informed by Messrs. Morgan Brothers, of Battersea, near London, that they now supply the crucibles used at the Melbourne Mint for this purpose, as well as the clay-pipes and plumbago crucibles.] They are fitted for use by filling them with a boiling aqueous solution of borax, letting it remain in for 10 minutes, then pouring it out, and afterwards drying them. When crucibles thus prepared are heated to redness, the borax melts, glazes their inner surface, and so makes them, as previously stated, impervious to molten chloride of silver. When used, they are placed within plumbago crucibles, with a view to prevent loss of gold in the event of their cracking, which, however, seldom happens. They are provided with loosely-fitting clay covers, each having two holes bored through, one in the centre for the passage of the chlorine pipe, and the other fitted with a plug, on the removal of which the contents of the crucible may be observed: the holes are $\frac{3}{4}$″ in diameter.

CHLORINE PIPES.—Common clay tobacco-pipe stems answer well: but pipes expressly made at the Battersea Crucible Works are now used, 22″ long, $\frac{1}{2}$″ in diameter, and $\frac{3}{16}$″ in bore. Two pipes may be used at a time in one crucible. Formerly, these pipes tapered slightly at one end, and were pierced with six fine holes at a distance of $\frac{1}{2}$″ from the other end, or that to be plunged into the molten gold. The lower end of the pipe should be heated for about 10 minutes immediately before use, for if not it is apt to split.

CHLORINE GENERATORS.—The best glazed stoneware acid jars, capable of holding from 10 to 15 gallons, and having two necks, are used. [Those shown in fig. 68 have three necks.] One of the necks is fitted with a sound cork, or, if obtainable, a vulcanized india-rubber plug, through which pass tightly two glass tubes, one the eduction tube, a few inches long; and the other the safety or pressure tube, 8′ or 10′ long, which may be formed of shorter tubes, united by vulcanized india-rubber joints. The other neck of the jar, which is intended for the introduction of the materials necessary for the generation of chlorine, is fitted with a leaden plug, covered with a short piece of india-rubber tubing to ac-

vasher; and as this plug has to withstand considerable pressure within, it must be well secured. On the bottom of the jar is d a draining layer, so called, of small quartz pebbles, nearly bottom of which the pressure tube descends; and upon this are placed from 70 to 100 lbs. of black oxide of manganese, in s of about $\frac{1}{4}''$ cube, and freed from powder by sifting, hydro- ic acid being the other ingredient used for producing the

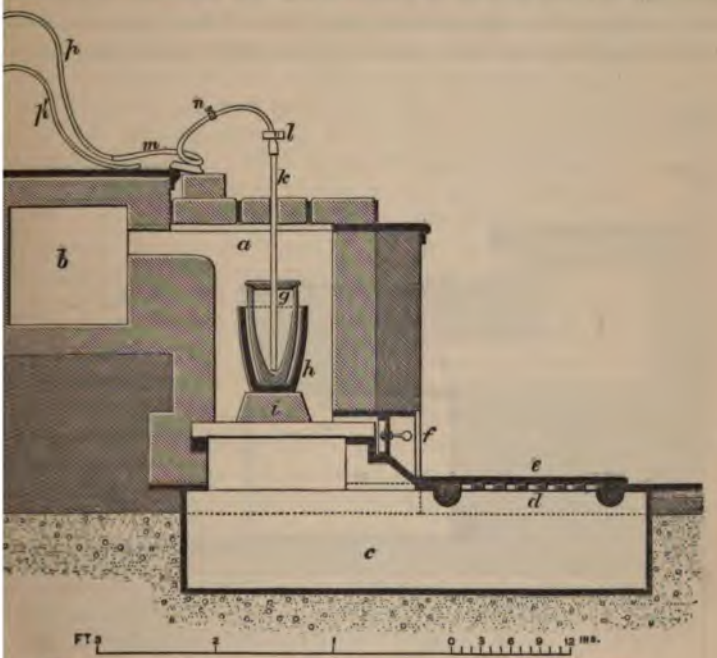

Fig. 66. Vertical section of a chlorine refining furnace. The lighter shading indicates fire-brick.

a. Body of the furnace.
b. Main flue communicating with a row of furnaces, and leading to a high chimney.
c. Ash-pit, consisting of a cast-iron box open at the top.
d. Movable lattice grating of cast-iron over the front of the ash-pit.
e. Movable cast-iron plate covering *d*.
f. Damper of cast-iron.
g. Clay crucible in which the gold is melted.
h. Plumbago crucible in which *g* is set.
i. Crucible stand of fire-brick.
k. Chlorine pipe of fire-clay.
l. Weight to keep *k* depressed in the molten gold.
m. Vulcanized caoutchouc tube.
n. Clip or compressor for regulating supply of chlorine.
o. Main lead-pipe connected with chlorine generators.
o'. Spare main lead-pipe to be used if necessary.
p. Branch lead-pipe from *o* and connected with vulcanized tube *m*.
p'. Duplicate of *p*.

ine. This quantity of oxide of manganese is sufficient for many ings, and will render unnecessary frequent dismantling of the ratus for charging. Each generator should be suspended to t half its height in a water-bath made of galvanized iron, and d by gas-burners underneath. Above the generator there is a l connected with the top of the safety or pressure tube, which is enough to receive all the liquor that may be forced up from the

generator, when the apparatus is in action and the passage of chlorine through the eduction pipe is stopped. The chlorine gas from the generator is conducted into a leaden pipe, fitted with branches for several furnaces respectively, all intermediate connections being formed by means of vulcanized india-rubber tubing. All joints between the various pipe and india-rubber tubes are easily secured, and made perfectly gas-tight, with a cement consisting of a thin solution of india-rubber in chloroform. By means of screw compression clamps or compressors on the india-rubber tubes, the supply of chlorine gas is regulated according to requirements, and stopped as

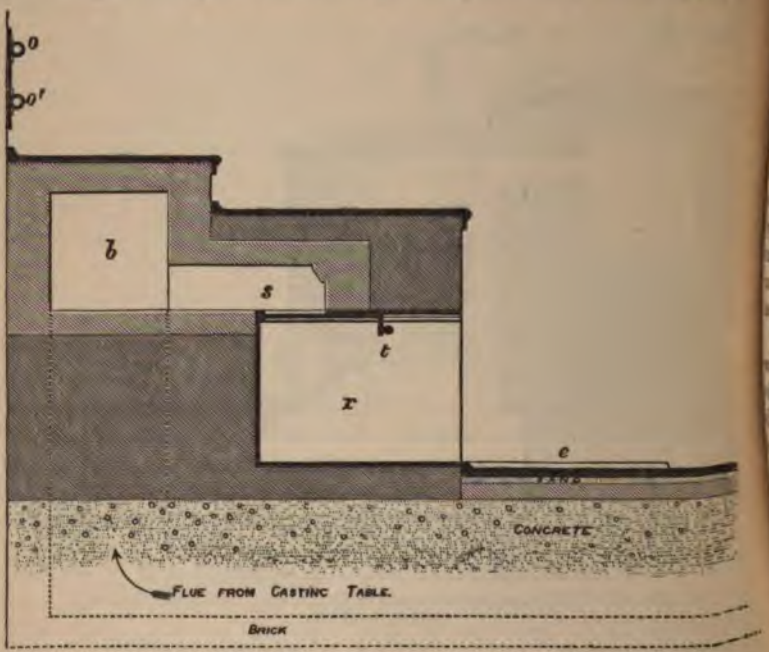

Fig. 67. Vertical section of a chlorine refining furnace through the fume-chamber.

b. Main flue.
c. Movable cast-iron plate.
r. Fume-chamber.
s. Flue from the fume-chamber to the main flue.
t. Wrought-iron damper.
o. Main lead-pipe.
o'. Spare main lead-pipe.

soon as the refining is over. When this stoppage occurs, the chlor[illegible]ne, accumulating in the generator, soon forces all the liquor contained [illegible] in it up the safety-tube into the vessel placed above to receive it. W[illegible]th two such generators as those above described, and three ordina[illegible]ry gold-melting furnaces, about 2000 ozs. of gold, containing about 1[illegible]% of silver, may be refined daily in the course of five hours. The[illegible]se generators are stated to be very convenient and manageable, a[illegible]d Miller doubts whether, if a suitable gas-holder could be made, [illegible]t would be preferable to them.

Mode of conducting the Process.—The crucibles are slowly and carefully heated to dull redness, and the gold is introduced in the

form of what are termed "slipper-shaped" ingots, two of which, placed face to face, with the narrow ends downwards, fit conveniently into one crucible.[1] This form of ingot is used with a view to prevent the crucibles from being split towards the bottom, which, it may be presumed, has been found to occur in the case of rectangular ingots. As soon as the gold is melted, but not before, from 2 to 3 ozs. of molten borax are poured upon its surface; for, if added previously, it acts too much on the lower part of the crucible, and, if thrown in cold, it is apt to chill the gold. The clay-pipe is now introduced; and at the moment when it reaches the molten gold, the screw compressor on the vulcanized india-rubber tube is slightly loosened, so as to allow a small quantity of chlorine gas to pass through, and thereby prevent any of the gold from rising and solidifying in the pipe. This done, the pipe is gradually depressed until it touches the bottom of the molten gold, where it is kept by means of a weight at the top, after which the compressor is quite relaxed, when the gas is heard bubbling up quietly through the molten gold, without causing any projection of globules. Sufficient hydrochloric acid must be introduced into the generator from time to time to maintain a rapid evolution of chlorine. Generally 1 imperial quart of acid, of 1·5 sp. gr., is allowed for every 10 ozs. of silver in the gold operated upon.

When the chlorine gas first passes into the molten gold, fumes escape from the holes in the lid of the crucible, which consist of the volatile chlorides of some of the baser metals, and not of chloride of silver, and which are particularly dense when much lead is present in the gold. When a cold body is placed in these lead fumes, a white deposit is formed upon it. After a time, which varies with the proportion of base metals in the gold, the fumes cease. So long as any sensible quantity of silver remains in the molten gold, the whole, or nearly the whole, of the chlorine continues to be absorbed; and the quicker the supply of chlorine, the shorter is the operation. Miller directs attention to the curious fact, that when corrosive sublimate is used the whole mass of gold is toughened by its action, although it is only thrown upon the surface of the metal; whereas, when chlorine gas is used for that purpose, it seems essential that the gas should pass to the very bottom in order to effect complete refining.

When the operation is nearly over, fumes of a darker colour than those produced at the beginning make their appearance; and the end of the refining is indicated by a peculiar flame or luminous vapour of a brownish-yellow colour, due to the escape of free chlorine at this period, as may be seen on removing the plug from one of the holes in the crucible lid. But this appearance is not of itself a sufficient indication that the operation is finished; for it is not completed until this flame imparts a peculiar reddish or

[1] The two ingots placed face to face, i.e. with their upper or flat surfaces in contact, form a solid of the same shape as the interior of the crucible.

brownish-yellow stain to a piece of white tobacco-pipe, or other similar substance, when it is held in it for a moment, and so long as any other colour is thus imparted to the piece of pipe, the refining is unfinished. When the signs indicating the termination of the process are observed, which, in the case of gold containing about 10% of silver, usually appear in about an hour and a half after the introduction of the chlorine, the current of gas is stopped, the clay crucible is lifted out of the plumbago one, and left exposed until the gold has solidified, which occurs after the lapse of 7 minutes. The liquid red-hot chloride of silver is then poured into iron ingot-moulds, previously very carefully dried and heated, as the slightest moisture would cause it to be violently projected about, to the great risk of bystanders. The crucible containing the gold, which is still red-hot, is inverted on an iron-table, when the metal falls out: the gold is now fine, and only requires to be re-melted and cast into bars. But 2% of the gold remains in the cake of chloride of silver, from which it is extracted in the manner to be presently described. Gold, containing 10% of silver and 1% of base metals, yields, on an average, by the chlorine process, a cake of chloride of silver, weighing, together with a little adherent borax, 16 ozs. for every 100 ozs. of gold operated upon.

The chloride of silver is melted in a clay crucible, prepared with borax, along with from 8% to 10% of laminated metallic silver of about $\frac{1}{8}$" thick. As soon as thorough fusion has occurred, the crucible is removed from the furnace and left to stand for about 10 minutes, after the lapse of which the still liquid chloride of silver is poured into large iron moulds, so as to form slabs of suitable thickness for treatment in the reduction process. The gold which was in the chloride of silver alloys with the metallic silver added, and collects into a button at the bottom of the crucible. The fusion of the slab of chloride of silver with metallic silver does not remove every trace of gold; but, with proper care, the quantity of gold remaining in the separated silver need not exceed 3 parts in 10,000, or about 2 grs. per lb. troy of silver, an amount too small to admit of its being extracted at Sydney with profit.

Method of reducing the Chloride of Silver.—The method adopted at the Sydney Mint was proposed by Mr. A. Leibius, fellow-assayer of Mr. Miller at that mint.[2] "The reduction," writes Leibius, "has always been effected in the usual manner, viz. by placing the slabs of fused argentic chloride between plates of wrought-iron or zinc, with the addition of acidulated water. Although a perfect reduction to metallic silver has always been effected, yet it required a considerable amount of time and manipulation, because the thick slabs of fused argentic chloride were, aft

[2] This method is described in a paper communicated by Leibius to the Royal Society of New South Wales, December 1st, 1869, and published in their Transactions; from which paper the information given in the text has been derived. have altered a word here and there the extracts within inverted commas have had no difficulty in construc the apparatus from this description.

two or three days, only partially converted into metallic silver, and had to be re-arranged in order to hasten their complete reduction. Such manipulation, however, was not only found to be very objectionable on account of the time which it required, but more so on account of the very disagreeable nature of the work. The reduced spongy silver had to be broken up by hand into small pieces, in order to ascertain if reduction were complete, and then boiled in acidulated water to free it from iron or zinc. It was, therefore, a desideratum to reduce the fused masses of argentic chloride more quickly, and to avoid the manipulation above mentioned."[3]

The principle which Leibius adopted is that upon which, in 1868, Messrs. De la Rue and Hugo Müller constructed their galvanic battery, in which fused chloride of silver is used as one of the elements, the other being zinc.

The following is the description of the apparatus contrived by Leibius:—Two thick boards, each 15″ long, are joined together at both ends by three strong battens, so as to form a frame, open at the top and bottom, 13″ long, 14″ wide, and 15″ deep, inside measure. In each of the boards forming the sides of this frame, there are seven vertical grooves, extending 12″ from the top, $\frac{1}{2}$″ wide and $\frac{1}{2}$″ deep, at intervals of $1\frac{1}{2}$″ from each other. At the lower ends of these grooves, along the whole length of the boards, there is a narrow horizontal groove, $\frac{1}{2}$″ deep, into which a strip of metallic silver, $\frac{1}{2}$″ wide and about as thick as a threepenny piece, is tightly fixed, projecting outwardly from one end of the frame about 18″. Zinc plates, $\frac{1}{2}$″ thick, a little less than 15″ long, and 12″ high, are dropped into the grooves, respectively, where they rest on the strips of silver: a connection is thus established between the zinc plates and those strips. The second part of the apparatus consists of a wooden frame, of the same length as the frame holding the zinc plates, but 3″ narrower; it is cut out of a board 1″ thick, and is provided with two handles; on each side of this second frame there are 12 slits, each $\frac{1}{2}$″ long; and through each series of these slits there passes a continuous band of silver, $\frac{1}{2}$″ broad and of the thickness of a threepenny piece, so as to form on each side of the frame six loops, $1\frac{1}{2}$″ long and $\frac{7}{8}$″ wide, the six loops on one side being exactly opposite those on the other side, respectively, and about 9″ apart. In these loops are placed the slabs of argentic chloride, which are 12″ long and 10″ high, and about $\frac{3}{4}$″ thick, and project at each end about 1″ beyond the bands of silver. The whole frame contains six of these slabs, which are placed in the spaces between the seven zinc plates, from which they are about $\frac{1}{4}$″ apart on each side. The projecting ends of the two horizontal strips of silver, jammed into the sides of the first or lower frame, are then connected with the ends of the silver forming the loops, in which the slabs are suspended

[3] I presume that the artificers at the Sydney Mint were more particular than practical metallurgists are generally found to be.

and the whole apparatus so arranged is placed in a tub filled with water. After a short time, galvanic action is discernible, and the liquid gets gradually warmer, when a strong current is observed. After about 24 hours, the action has nearly ceased, and the reduction of the whole of the argentic chloride is found to be complete, the resulting metallic silver remaining in the loops, and presenting outwardly nearly the same appearance as the original slabs of chloride. As the chloride of silver contains always more or less chloride of copper, this is reduced along with the former, whilst the latter acts as an exciting liquor in the reduction apparatus.

In the first experiments, a weak solution of common salt was used as exciting liquor; but it was found that it could be dispensed with, and that common water was sufficient. The action, however, with water alone, is a little retarded, and does not become powerful until about 2 hours after the apparatus is charged. By using a part of the liquor resulting from a previous reduction of argentic chloride, and which contains chloride of zinc, it has been found that galvanic action sets in very rapidly, and hastens thereby the completion of the reduction. No acid is used, and therefore the amount of zinc consumed in each reduction has been found to be almost the same as would be theoretically required to combine with the chlorine of the argentic chloride treated with metallic zinc, in order to form chloride of zinc. The quantity of metallic zinc consumed has always been from 24% to 25% of the weight of the argentic chloride reduced.

The reduced silver is boiled in acidulated water, in order to remove the "basic [chlorides] and oxychlorides" (?), and finally in pure water, while still suspended in the silver loops. As soon as it is withdrawn from the last boiling, it is ready for melting, as the heat from the boiling water dries the porous mass of silver sufficiently for that operation. The seven zinc plates, before use, weigh about 140 lbs. avoirdupois, and the six slabs of argentic chloride, of the dimensions stated, about 140 ozs. troy. The zinc plates continue to be used until they become too thin, when they are re-melted and cast into fresh plates. It has been found that the quantity of zinc consumed is little, if at all, increased, by prolonging the time of connection with the silver plates after the reduction is completed; so that the whole apparatus, when once set in operation, may be left to itself until it is convenient to melt the reduced silver. The argentic chloride is reduced much more quickly in this apparatus than when it is simply placed in contact with iron or zinc plates, and any handling of the chloride from the time it has been put into the loops to that when it is ready for melting is unnecessary,—advantages which, according to Leibius, have been fully appreciated by those who had formerly to practise the tedious and disagreeable (!) manipulation previously mentioned.

Loss of Gold and Silver, and Cost of the Process.—According to Miller, the average loss of gold by the chlorine process up to December 1869 was 19 parts per 100,000 of gold treated, which is considerably less than would have resulted from the usual toughen-

ing with corrosive sublimate; and the loss of silver amounted to 240 parts per 100,000, in operating upon gold containing originally about 10% of silver. He expresses his belief that a considerable portion of the gold and silver thus lost might be recovered from the crucibles and ashes, remaining after the operation; and adds that "it is found that as manipulatory skill is acquired the proportional loss of silver appears to be decreasing. The cost of refining gold, containing 10% of silver, on the large scale, at Sydney, including labour and loss of gold and silver, but excluding rent of premises and superintendence, is (Dec. 1869) about 5 farthings per ounce; but it varies with the proportion of silver in the gold operated upon. The fineness of the gold after treatment by this process ranges from 991 to 997 per 1000, the average, deduced from the refining of many thousand ounces, being 993·5, or 23 carats $3\frac{3}{8}$ grains: the other $6\frac{1}{2}$ thousandths are silver. This result, Miller thinks, "compares favourably with any of the previously known practical processes, none of which leave less silver than this in the resulting fine gold." He further remarks that "if the refined gold be subjected to a re-refinage[4] by chlorine, the amount of silver left in it can be reduced to $\frac{2}{10}$ths per cent., just as in the refinage by the ordinary sulphuric acid process the same result can be obtained by subjecting the refined gold to a further refinage with bisulphate of potash." I venture to take exception to this statement: sulphuric acid is one thing, and bisulphate of potash another; in refining with the former the temperature does not exceed the boiling-point of sulphuric acid, whilst in further refining with the latter the temperature is much higher. Thus a re-refinage of argentiferous gold by chlorine is not comparable to a re-refinage of it by bisulphate of potash. But re-refinage with chlorine means passing chlorine through the re-melted gold, previously refined by that agent. What different effect, it may be asked, could be produced by such a repetition of the process, from that which would result from longer continuance of the passing of chlorine in the first instance?

The silver from the desilverization of gold by chlorine is said to be tough, but to vary somewhat in quality according to the kind of gold from which it has been derived. If the gold contain much copper, most of this metal remains in the resulting silver; but the other metals are nearly all eliminated. The fineness of the silver has ranged (up to December 1869) from 918·2 to 992·0 per 1000, the average being 965·5. The percentage composition of the silver separated by the chlorine process from gold, which contained copper, lead, antimony, arsenic, and iron, was found to be as follows:—

Silver	972·3
Copper	25·0
Gold	2·7
Zinc and iron	traces
	1000·0

[4] In the original paper it is "*re*finage," which is clearly a typographical error.

As the process of desilverizing and toughening gold by chlorine is of much practical importance, I append several official documents on the subject, for which I am indebted to my friend General Ward, R.E., Deputy-Master of the Sydney Mint.

REPORT ON EXPERIMENTAL REFINING BY MILLER'S CHLORINE PROCESS.

Royal Mint, Sydney Branch,
Sydney, April 13, 1869.

THE DEPUTY-MASTER, ROYAL MINT.

SIR,—We have the honour to inform you that, in accordance with your instructions, dated 8th August last, Mr. Miller's process of refining and toughening has received a practical trial by having been applied to the brittle gold imported into the mint during the quarter ending 31st March last; and that we are enabled to lay before you the following report.

Referring for the details of the experiments to table A annexed, the results may be summarized as follow:—

I. The amount of alloy operated on consisted of 30,672 ozs., which contained, according to assay, of—

	ozs.	Parts per 1000.
Fine gold	27,409 or	893·6
Fine silver	3,052 „	99·5
Base metals	211 „	6·9

II. The refined gold produced amounted to 27,620 ozs. of average assay of 991·56 parts per 1000, the two highest assays being 996 and 995. The gold was invariably perfectly toughened in the first part of the operation.

III. The amount of silver extracted was 2718 ozs. (this amount includes 18·592 ozs. of gold left in the silver produced) of average assay of 966·7 parts per 1000, while 233 ozs., or 7·63 per cent. of the whole amount of silver operated on, was left in the refined gold.

IV. The loss on the whole operation consisted of—

	ozs.
(A) Loss of gold	3·395
(B) Loss of silver	122·391

These amounts, calculated for the amount of gold-alloy operated on, show the proportional loss to be of—

Gold	11 parts per 100,000.
Silver	399 „ „

Although not taken into account, this loss of gold and silver is considerably reduced by the amount of those metals found, according

to assay, to have been left in the tailings from the amalgamatio
the pots and ashes (see table A), as well as that contained in the
recovered from the flue of the refining furnace, the particula
which are as follow:—

(A) Assay of tailings from amalgamation of pots and a
which were found to contain of—

	ozs.
Gold	1·249
Silver	34·608

(B) Assay of stuff from the short horizontal flue belonging t
refining furnaces, which was found to contain of—

	oz.
Gold	0·441
Silver	0·853

It is more than probable that the remainder of the flue, as w
the bottom of the chimney, contains also a small amount of
metals.

The following is a full description of the whole process as ad
in these experiments.

The preliminary operations include the boraxing of the me
pots and the charging of the chlorine generators.

About 100 French white clay pots of Nos. 14, 15, 16, and 20
filled with a hot solution (concentrated) of borax, which was all
to remain in them for about 10 minutes, when it was poured off
pots when dry presented a thin coating of crystallized borax o
inner surface.

Two chlorine generators were employed; they consisted o
best glazed earthenware acid jars of 10 to 15 gallons' capacity,
tap holes at the bottom and well-ground openings at the top, to
[latter] were fitted, with india-rubber washers, well-ground leade
strengthened with cast-iron backings. The lids contained two
ings, one closed with a cork and holding the safety and de
tubes, the other for charging the oxide of manganese, capa
being closed with a leaden plug covered with an india-rubber w
The lids were well secured by being screwed to iron bands pa
under the bottom of the jars. The corks holding the safet
delivery tubes were made perfectly gas-tight by means of a
coating of melted sealing-wax.

The generators were heated by means of galvanized-iron
baths (under which were gas-burners), and were suspended b
bands to about half their height within the water-baths.
generator was charged with a layer of quartz pebbles, through
the safety-tube passed; on this layer was poured from 750 to 10
of binoxide of manganese in small pieces (about ¼ inch) free
powder, the hydrochloric acid being supplied through the safety
which stood about 8 feet above the top of the generator. By
of india-rubber tubing attached to the top of the safety-tube, th
when no longer required could be driven up into a receiver an
over again in future operations.

The chlorine gas from the generators passed into a leaden pipe, fitted with branches of the same material, opposite each generator and each furnace. The gas was then conveyed through india-rubber tubing of ¼ inch diameter to the clay-pipes, which passed through a hole in the loosely-fitted lid to the bottom of the pot containing the melted alloy.

In order to ensure perfectly tight joints between the india-rubber tubing and the lead, glass, and clay-pipes, a cement was used consisting of a thin solution of caoutchouc in chloroform. By means of screw-clamps applied to the india-rubber supply-tubes, the chlorine gas could be regulated and more or less shut off according to requirements. For quantities of about 400 ozs. of gold of about 890 assay, a No. 16 pot was used, which, as a precautionary measure, was placed three-fourths of its height within a black-lead pot. The gold potted at 9 A.M. was ready for the chlorine gas at about 10.15 A.M. It has been found advantageous to add from 3 to 4 ozs. of fused borax to the melted gold previous to inserting the chlorine pipes, since if borax is added before the gold is melted it acts too much upon the lower portions of the pot.

The chlorine gas was supplied to each pot by one or sometimes by two clay-pipes, and the supply of gas kept up by repeated additions of common hydrochloric acid through the safety-tube. The refinage of 400 ozs. of gold of the fineness of about 900 required about two Winchester quarts of hydrochloric acid. The pressure of gas was indicated by the height of the column of acid in the safety-tube, which also afforded a ready method of regulating the supply of chlorine, or of detecting any leakage or breakage in the clay-pipes or crucibles. The average height of the column of acid was about 84 inches for 400 ozs. of gold, or 20 inches for every inch of melted gold in the pot.

The time required to deliver sufficient chlorine to refine about 400 ozs. of gold of 900 assay, was found to be from 1 to 2 hours, according to the size of the pipes employed and the rate at which the gas was generated.

On the first introduction of the chlorine pipes, which have to be carefully and gradually heated and the gas allowed to pass through them while being immersed in the molten gold, a quantity of fumes escape (the chlorides of some of the baser metals contained in the gold). These fumes cease after some time, while the end of the refinage is indicated by other fumes, accompanied by a peculiar flaming, which may be observed on removing a small plug which fits into a hole in the lid of the pot. The end of the operation is further *and chiefly* shown by a characteristic reddish-brown colour which is imparted to a clay-pipe, when held over the hole before mentioned, and exposed to the escaping fumes for a few seconds.

When these phenomena occurred, the gas was shut off, and the crucibles taken out of the furnace. The lid was then removed, the white pot lifted out of the black one and allowed to stand for 7 minutes, when the liquid argentic chloride was poured into iron

moulds, while the gold which was solidified in the crucible fell out in the shape of a cone soon after the pot was turned upside down on the iron table. The lump of gold was then slightly scraped, and at once plunged into a strong solution of sodic chloride, to free it from the little argentic chloride adhering. The salt bath was kept in a wooden tub, and all contact avoided with any metals which would reduce any of the silver on the surface of the gold. The refined gold so obtained and cleaned was re-melted and poured into ingot-moulds.

The argentic chloride obtained contained a considerable quantity of gold, averaging 2 per cent. on the amount operated upon, and which appears to be chiefly in a state of combination with chlorine and probably silver.

To free the argentic chloride from the gold, it was melted (covered with a layer of fused borax) in a boraxed clay-pot, with the addition of about 10 per cent. of silver rolled to the thickness of a florin. As soon as the whole was thoroughly melted, the pot was taken out of the furnace and allowed to stand for about 10 minutes; the argentic chloride was then poured into large iron pans, and the button of silvery gold remaining at the bottom of the pot was re-melted together with the scrapings and the addition of a little soda. [Carbonate of soda, doubtless.]

By these means it was not found possible to remove the whole of the gold contained in the argentic chloride; on an average about 7 parts in 1000 were left in the reduced silver, and the proportion was never less than 2 parts of gold to 10,000 parts of the reduced silver.

The argentic chloride thus obtained was readily reduced between iron plates in the usual way.

The alloy operated upon was treated in 73 separate pots, containing on an average 420 ozs. each, this amount being regulated by the assay of the gold and the size of the pot employed.

Working on gold of an average fineness of 890, it was found convenient, with the appliances at our disposal, to refine two pots in a working day (9 A.M. to 4 P.M.), and to deliver within those hours about 98 per cent. of the gold contained in the alloy operated on, in a refined state, the remainder being retained in the argentic chloride as already described.

Working with two chlorine generators, each charged with from 750 to 1000 ozs. of binoxide of manganese, of about 80 per cent. [*i.e.* containing that percentage of the pure oxide], the former required but three charges of manganese, the total quantity used being about 300 lbs., and that of hydrochloric acid 10 cwt. Under these circumstances 6 parts of hydrochloric acid have chloridized [the American expression is chlorinize, which, I think, is better.—J. P.] about 1 part of silver besides the base metals contained in the alloy operated on, and allowing for all waste of gas.

Only a very slight smell of chlorine was observed during the operation of refining; the only time when chlorine was distinctly perceptible, though without marked inconvenience to those en-

gaged, was during the pouring of the argentic chloride as already described.

From table B (also annexed) it will be seen that the total expenses incurred in carrying out these experiments (exclusive of plant) amount to £112 17*s.* 10*d.*, being at the rate of about one penny per ounce on the weight of the alloy operated on.

In these expenses the labour of one man only has been charged, the superintendence and occasional assistance required having been supplied by the regular mint staff.

The outlay for two additional furnaces, chlorine generators, and sundries, forming a small permanent plant, was under £50, on account of which £5 has been charged for wear and tear.

While the loss of gold in these experiments is duly taken into account, no notice is taken either of the loss of silver, or of the amount of silver left in the refined gold, since, under present circumstances, the silver does not appear as any actual loss to the mint.

In considering the expenses incurred in toughening and refining these 30,672 ounces of gold it is but fair to take into account the cost which would have been entailed in toughening the same by corrosive sublimate, the process hitherto employed, by which no silver is obtained, and which may be stated as not less than £50. The whole of the brittle gold which is likely to be received at the mint can be toughened and refined with a slight extension of the present plant.

This, with a small additional refinage of tough silvery gold, would admit of all the bullion being brought to an average fineness of, say, 23 carats, thus ensuring a uniform mixture of equal parts of silver and copper forming the alloy in the standard bars prepared for coinage, as has been the case during the past quarter, and the advantages of which it is unnecessary to enumerate.

We are moreover of opinion that the cost of additional plant, labour, and materials required in order to be able to refine the whole of the gold received by the mint, would be more than fully repaid so long as the gold contained 3 per cent of silver.

We have the honour to be, Sir,

Your most obedient servants,

ROBERT HUNT, *Melter.*
A. LEIBIUS, *Assayer.*

A.—Results of Experiments in refining Gold by Miller's Chlorine Process, stated in Troy Ounces.

Brittle gold operated on.						Refined ingots produced.						Silver extracted.				Ends.‡				Apparent waste in operating.				Remarks.
Gross weight.*		Containing by assay				Gross weight.		Containing by assay				Gross weight.		Containing by assay		Containing by assay				Gold.		Silver.		
		Gold.		Silver.				Gold.		Silver.†				Gold.		Silver.								
1216	45	1102	892	97	010	1115	06	1095	750	19	310	73	20	6	600	61	317					542	16	383	Excessive loss of silver accidental.
404	20	357	232	45	513	350	64	348	711	1	929	41	85		925	40	586	7	263		337	333	2	661	
1346	50	1246	320	91	158	1244	51	1233	309	11	201	74	00		200	69	116	11	581	2	759	1 230	8	082	
2649	85	2384	802	243	819	2362	59	2345	296	17	294	197	30		830	183	483	37	817	18	813	859	24	229	
1769	40	1548	579	212	505	1538	11	1519	451	18	659	187	30	4	609	181	742	23	300	6	450	1 219	5	654	
1889	00	1698	022	178	699	1692	73	1679	610	13	120	155	65		202	148	599	16	830	5	770	1 380	11	210	
1365	50	1230	862	128	493	1226	16	1209	484	16	676	99	40		328	95	941	20	436	5	714	614	10	162	
651	55	572	191	76	622	564	96	558	011	6	949	63	00		435	62	370	13	231	4	349	514	2	954	
2774	15	2534	172	229	284	2507	40	2493	321	14	079	193	10		174	189	083	39	500	12	000	1 177	14	122	
994	15	906	864	77	941	900	90	894	233	6	667	67	00		067	60	173	12	266	4	334	298	6	767	
815	90	734	310	78	326	725	36	720	282	5	078	63	75		127	63	564	13	500	7	880	401	1	884	
3646	58	3092	204	532	251	3041	95	3019	721	22	229	458	20	2	062	449	448	64	718	25	632	5 703	34	942	
2024	70	1872	395	145	262	1874	53	1855	288	19	242	112	35		062	110	467	15	826	7	434	1 219	8	119	
1773	58	1518	604	244	779	1493	18	1482	080	11	100	210	00		210	207	613	35	279	12	171	1 035	13	895	
677	50	599	045	74	457	593	58	588	831	4	749	63	65		099	61	877	10	004	3	216	111	4	615	
2371	05	2212	769	139	770	2203	83	2189	249	14	581	113	00		079	107	775	23	198	10	932	283	6	482	
4302	65	3798	559	456	318	3730	58	3707	743	22	837	413	05	1	623	403	433	84	801	21	729	4 392	8	319	
														18	592			429	550	149	440				
Ends delivered to Bullion office.....						454	377	447	021	7	356	132	55			131	198					1	121	10	886	Excessive loss of silver accidental.
30672	71	27409	822	3052	207	27620	447	27387	391	233	056	2718	35			2627	785	Total apparent waste				22	431	191	366	
																		Recovered by amalgamation of pots and ashes.....				19	036	68	975	
																		Loss in refining				3	395	122	391	

Mean assay of alloy operated on .. { Gold 893·6 / Silver 99·5

Mean assay of refined ingots..... Gold 991·56

Delivered to Bullion office 2619 883

Loss in re-melting and assaying.... 7 902

The alloy was melted in 73 pots. Average weight, 420 ozs. Mean assay of silver extracted, 966·7. Proportional loss on the gross weight of alloy operated upon ..... { Gold 11 parts / Silver 399 " } in 100,000.

* The lines dividing the figures under each head are substituted for decimal points. Thus taking the first number in the table, 1216 | 45 means 1216·45.

† Only assayed for gold; the difference being silver.

‡ Consisting of gold and silver extracted from chloride by fusion with metallic silver and scrapings of the pots, scraps, etc.

Robt. Hunt, *Melter*.
A. Leibius, *Assayer*.

B.

Results of Experiments in refining Gold by Miller's Chlorine Process.

Detail of Expenses for the Quarter ending 31st March, 1869.

Labour:—

	£	s.	d.
1 fireman, 13 weeks at £2 8s.	31	4	0

Fuel:—

	£	s.	d.				
Coke, 2½ tons at £2 10s.	6	5	0				
Charcoal, 20 bushels at 6d.	0	10	0		10	5	0
Gas, 7000 ft. at 10s.	3	10	0				

Pots, chemicals, etc.:—

French pots ....No. 20, 7 at 2s. 3d. ..	0	15	9				
„ .... „ 16, 80 „ 1s. 9d. ..	7	0	0	£	s.	d.	
„ .... „ 15, 30 „ 1s. 6d. ..	2	5	0	11	5	9	
„ .... „ 14, 10 „ 1s. 3d. ..	0	12	6				
French covers..... 25 „ 0s. 6d. ..	0	12	6				
Chlorine pipes				2	7	6	
Plumbago pots..No. 25, 5 at 8s. 4d. ..	2	1	8				
„ .... „ 20, 5 „ 6s. 8d. ..	1	13	4				
„ .... „ 16, 10 „ 5s. 4d. ..	2	13	4				
„ .... „ 12, 5 „ 4s. 0d. ..	1	0	0				
„ „ 8, 5 „ 2s. 8d. ..	0	13	4	10	15	5	
Plumbago covers „ 25, 5 „ 2s. 6d. ..	0	12	6				52 0 5
„ „ 18, 20 „ 1s. 9d. ..	1	15	0				
Plumbago stirrers ..... 5 „ 1s. 3d. ..	0	6	3				
Oxide of manganese, 3 cwt. at 4s. 6d. ..	0	13	6				
Hydrochloric acid, 10 cwt. at 4d. per lb.	18	13	4	19	6	10	

Sundries:—

Vulcanized india-rubber tubings and rings	6	0	5				
Borax, 16s. 4d.; salt, 5s.; plaster of Paris, 1s. 2d.	1	2	6	8	4	11	
Ammonia, 6s.; chloroform, 16s.	1	2	0				
							£93 9 5
Wear and tear on additional plant, say 10 per cent.				5	0	0	
Loss of gold in refining.....				14	8	5	19 8 5
Total cost of refining 30,672·10 ozs.							£112 17 10
Lowest estimated expense of toughening the same amount by means of corrosive sublimate.....							£50 0 0

B.

RESULTS OF EXPERIMENTS IN REFINING GOLD BY MILLER'S CHLORINE PROCESS—*continued.*

Memoranda respecting Silver.

	ozs.	ozs.	ozs.
Nett weight of fine silver contained in the alloy operated on (according to assay)			3052·207
Loss in refining	122·391		
„ re-melting and assaying	7·902		
Total loss of silver	130·293		
		130·293	
Silver left in refined ingots of gold		233·056	
Total weight unavailable		363·349	
Silver recovered from pots and ashes		68·975	
			432·324
Nett weight for sale			2619·883

Value at 5*s.* per ounce £654 19 4

NOTE.—The silver has been valued in all calculations at 5*s.* per oz. (fine), to allow for expenses of exportation, etc., etc.

Cost of the additions to melting-house:—

	£	*s.*	*d.*
Two new furnaces	10	0	0
Gas, water, and drain	10	0	0
Two generators fitted	15	0	0
Two water-baths	1	10	0
Gas-burners, lead pipes, etc.	6	0	0
Fittings for generators	5	0	0
Sundries, say	2	10	0
	£50	0	0

ROBT. HUNT, *Melter.*
A. LEIBIUS, *Assayer.*

CONTINUATION REPORT ON EXPERIMENTAL REFINING BY MILLER'S PROCESS.

Royal Mint, Sydney,
July 10, 1869.

THE DEPUTY-MASTER,

SIR,—Referring to our report of 13th April last, we have the honour to submit the following results of the continued working of the new refining process during the quarter ended 30th June.

I. The amount of alloy operated on consisted of 40,373·10 ozs., containing—

	ozs.	Parts in 1000.
Fine gold	36,065·551	or 893·3
Fine silver	3,845·207	„ 95·2
Base metals	462·342	„ 11·5

II. The refined gold produced amounted to 36,005·24 ozs. of 993·12 average assay per 1000.

III. The amount of silver extracted was 3,487·20 ozs., containing—

	ozs.
Fine silver	3,363·939
Fine gold	4·587

The average assay of the silver produced being 964·6, while 247·459 ozs., or 6·43 per cent. of the whole amount of silver operated on, were left in the refined gold.

IV. An unrefined portion of alloy (ends), containing 296·776 ozs. per 1000 of fine gold and 136·602 ozs. of fine silver, has been left for treatment during the present quarter.

V. The loss on the whole operation consisted of—

	ozs.
a. Loss of gold	7·907
b. Loss of silver.....	97·207

which, calculated on the quantity of gold alloy operated on, shows the proportional loss to be—

Gold about 19 parts in 100,000.
Silver „ 241 „ „

As in our former report, the above does not include the gold and silver left in the tailings from the amalgamation of the pots and ashes, and which consisted of—

a. Tailings from amalgamation of pots, containing by assay—

	ozs.
Gold	3·78
Silver	57·99

b. Tailings from amalgamation of ashes, etc., containing—

	ozs.
Gold	0·20
Silver	1·70

The above would considerably reduce the loss in both metals.

VI. While the proportional loss of gold during the quarter just ended has been larger than that during the previous three months, viz. 19 against 11 parts in 100,000, the loss of silver has been considerably smaller, being only 241 against 399 parts in 100,000 (both amounts being calculated on the quantity of alloy operated on).

The proportion of fine gold in the alloy has been exactly the same in both quarters; the proportion of silver has been rather less, and the proportion of base metals rather more during the last three months.

The quantity of silver unavailable (by loss in operating and by being left in the refined gold) was 344·67 ozs., or about 9 per cent. of the whole amount of silver contained in the alloy operated on. This proportion will be found to decrease with an increased quantity of silver in the alloy.

The refined gold produced was of somewhat higher average assay than that of the previous quarter, being 993·12 against 991·15 per 1000.

The plant and method of working have been generally the same as detailed in our former report.

The treatment of the argentic chloride for the purpose of freeing it from gold has, however, been much more uniform in its results; and although in no instance has the silver produced been free from gold, the amount of the latter has varied only from 3 to 27 parts in 10,000, the average being 13 in 10,000 parts of the silver bullion produced.

The quantity of the silver and base metals operated on being 4307·549 ozs., the mixed chlorides of silver, copper, etc. produced (including a portion of borax) weighed 6160 ozs. and were melted in white pots (about 280 ozs. to each pot). There were added 448 ozs. of metallic silver (or about 7 per cent. of the weight of the chlorides) in order to free the chlorides from the gold which they contained.

The total amount of gold thus extracted was 666·620 ozs., while 4·587 ozs. were left in the reduced silver, making the total amount of gold originally left in the chlorides 671·207 ozs.

On referring to the annexed detail of the expenditure, it will be seen that the cost of refining, including gold lost in operating (but no silver), has been £153 6*s.* 6*d.*, or rather less than one penny per ounce of gold of 890 assay per 1000, the proportional cost in both quarters being very much the same.

In treating gold alloys containing a large proportion of silver, such as New Zealand Thames gold, or those alloyed with base metals, the expenses of refining by this process will be found to increase with the quantity of silver or base metals contained in the alloy.

We have the honour to be, Sir,

Your most obedient servants,

(Signed) ROBERT HUNT, *Melter.*
A. LEIBIUS, *Assayer.*

EXPERIMENTAL REFINING BY MILLER'S PROCESS.

Detail of Expenses for the Quarter ending 30th June, 1869.

Labour:—							£	s. d.
1 fireman, 13 weeks at £2 14s.							35	2 0
Fuel:—								
			£	s.	d.			
Coke, 3½ tons at £2 10s.			8	15	0			
Charcoal, 25 bushels at 6d.			0	12	6		16	12 6
Gas, 14,500 ft. at 10s.			7	5	0			
Pots, chemicals, etc.:—								
French white pots	No. 20, 18 at 2s. 3d.		2	0	6			
„ „ „	18, 13 / 17, 37 at 2s.		5	0	0	£ s. d.		
„ „ „	16, 30 at 1s. 9d.		2	12	6	14 6 9		
„ „ „	14, 35 „ 1s. 3d.		2	3	9			
White clay covers	100 „ 6d.		2	10	0			
Chlorine pipes						6 0 0		
Plumbago pots....	No. 30, 2 at 10s.		1	0	0			
„ „ „	25, 2 „ 8s. 4d.		0	16	8			
„ „ „	20, 2 „ 6s. 8d.		0	13	4			
„ „ „	18, 3 „ 6s.		0	18	0			
„ „ „	16, 6 „ 5s. 4d.		1	12	0			
„ „ „	14, 6 „ 4s. 8d.		1	8	0		63	0 3
„ „ „	10, 10 „ 3s. 4d.		1	13	4	9 17 2		
„ „ „	2, 6 „ 8d.		0	4	0			
„ „ „	1, 4 „ 4d.		0	1	4			
„ lids	18, 6 „ 1s. 9d.		0	10	6			
„ „ „	14, 3 „ 1s. 6d.		0	4	6			
„ „ „	10, 3 „ 1s.		0	3	0			
„ stirrers	10 „ 1s. 3d.		0	12	6			
Oxide of manganese, 2½ cwt. at 6s.			0	15	0	27 16 4		
Hydrochloric acid, 14½ cwt. at 4d. per lb.			27	1	4			
Sundries:—Fluxes, tubing, etc.						5 0 0		
							£114	14 9
Wear and tear of plant, say 10 per cent. on £50						5 0 0	38	11 9
Loss of gold in refining						33 11 9		
Total cost of refining 40,373·10 ozs.							£153	6 6

(Signed) ROBERT HUNT, *Melter.*
A. LEIBIUS, *Assayer.*

F. Bowyer Miller's Process of refining and toughening Gold by Chlorine Gas.

Results of the Operations of the year 1869 from refining by Chlorine in the Sydney Mint.

			ozs.
Gold alloy operated on	Gross weight		202,662·990
Containing by assay	Pure gold		181,946·194
	„ silver		18,688·734
		Per 1000.	
Average assay of alloy	Gold	897·8	
	Silver	92·2	
	Base metals	10·0	
Refined gold produced	Gross weight		182,523·027
Containing by assay	Pure gold		181,272·370
	„ silver		1,250·657
Average assay of refined gold (including preliminary trials and incomplete operations)		993·1	
Silver bullion extracted	Gross weight		17,329·090
Containing by assay	Pure silver		16,723·117
Average assay of silver bullion		965·0	
Apparent waste in operating	Pure gold		22·341
	„ silver		374·493
Gold alloy remaining unrefined and carried over, containing by assay	Pure gold		651·483
	„ silver		340·467

Nett value in the colony of the silver produced..... £1320 2 9

Note.—The "waste in operating" would be much reduced if allowance were made for the gold and silver *recoverable* from the sweepings, etc., which, although once amalgamated, would still yield not less than 3 ozs. of gold and 100 ozs. of silver.

F. Bowyer Miller's Process of refining and toughening Gold by Chlorine Gas—*continued.*

Details of Expenses incurred during the year 1869, *in refining by Chlorine in the Sydney Mint.*

	£	s.	d.	£	s.	d.
Labour				136	10	0
Fuel:—						
Coke, 13 tons	32	10	0			
Charcoal, 105 bushels	2	12	6			
Gas, 36,500 cubic feet	17	2	6			
				52	5	0
Chemicals, crucibles, etc.:—						
French pots and covers	55	1	3			
Chlorine clay-pipes	12	6	0			
Plumbago pots, covers, etc.	38	10	10			
Oxide of manganese, 12½ cwt.	3	13	6			
Hydrochloric acid, 3½ tons	103	4	8			
Fluxes, tubing, and sundries	31	0	11			
				243	17	2
Wear and tear of plant, say				20	0	0
Total expenses (exclusive of waste) of refining 202,663 ozs.				£452	12	2

Waste in operating:—	ozs.	£	s.	d.	£	s.	d.
Gold lost in refining (fine)	22·341	94	18	0			
Deduct gold recoverable from the sweepings, etc. (fine)	3·000	12	14	9			
Total value of gold lost					82	3	3
Silver lost in refining (fine)	374·493	92	12	5			
Deduct silver recoverable from sweepings, etc.	100·000	25	0	0			
Total value of silver lost					67	12	5
					£149	15	8
Total cost of refining 202,663 ozs., including loss of gold and silver					£602	7	10

The cost of toughening the above gold by the usual corrosive sublimate process, by which no silver would have been recovered, would have been (inclusive of waste of gold, etc.) not less than £300 0 0

Therefore £4320 worth of silver were saved by an extra cost of..... £302 7 10

Note.—Before the introduction of the chlorine method no gold was refined in the colony, the price of acids, etc., in Australia being too great to leave sufficient margin of profit on the operation.

GOLD REFINING BY F. BOWYER MILLER'S CHLORINE PROCESS AT THE ROYAL MINT, SYDNEY.

During 1870 :—

		ozs.
Amount operated on		239,650·62
Average assay before operation	Gold 907·4 in 1000 parts.	
	Silver 82·2 „ „	
Mean assay of refined gold produced..	993·9 „ „	
Mean assay of silver produced	964·5 „ „	
Loss in operating	Fine gold	18·325
	„ silver	27·287

During the first half of 1871 :—

		ozs.
Amount operated on		283,528·45
Average assay before operation	Gold 857 in 1000 parts.	
	Silver 127 „ „	
Mean assay of refined gold produced..	993·6 „ „	
Mean assay of silver produced	923·0 „ „	
Loss in operating	Fine gold	45·66
	„ silver ..	No loss, but a small gain (apparently).

NOTE.—The apparently increased loss of gold in the two quarters of 1871 arises from the fact that the Sydney Mint has paid the public since January 1871 to the fourth place of decimals in the assay, instead of the third as heretofore.

EGULATIONS BEFORE THE ADOPTION OF THE METHOD OF REFINING BY CHLORINE, WHEN NO SILVER WAS ALLOWED FOR.

The Treasury, New South Wales,
June 30, 1869.

REGULATIONS FOR THE RECEIPT OF GOLD FOR COINAGE AT THE SYDNEY BRANCH OF THE ROYAL MINT.

His Excellency the Governor, with the advice of the Executive ouncil, has been pleased to frame the following Regulations for the eceipt and coinage of gold at the Sydney Branch of the Royal Mint, —such regulations to take effect from 1st July next.

1. Importations of gold-dust or gold-bullion for coinage, from 0 ounces upwards, will be receivable at the Mint daily (Saturdays nd holidays excepted), between the hours of 11 A.M. and 3 P.M.

2. In addition to the charge of threepence per ounce, imposed by Her Majesty's Proclamation of the 3rd February, 1866, on the coinage of gold, there shall be paid for melting, assaying, and refining, the following charges, viz. :—

(1.) On undivided parcels, containing not less than one thousand ounces standard (to be melted and assayed in one lot), at the rate of threepence per ounce (standard).

(2.) On parcels containing less than one thousand ounces standard, at the rate of fivepence per ounce (standard).

3. A reduction of the above Mint charges, to the amount of threepence per ounce standard, will be made in respect to gold, the produce of any other country, imported to the Mint, under the conditions prescribed in the second clause of the Act, 26 Vict., No. 5, granting a duty on gold.

4. The value of the bullion will be determined on the reports of the Mint Assayers.

5. The gold will be melted, if preferred, in the presence of the importer. The importer will also be furnished, on demand, with a clip for assay, from his own ingot, as a check on the reports of the Mint Assayers.

6. Gold received up to Wednesday evening in each week will be payable on the following Tuesday. Gold received after Wednesday will be payable on the following Tuesday week.

7. The Mint will issue, if required, gold-bullion in bars or ingots, at £3 17*s.* 10½*d.* per ounce, standard.

SAUL SAMUEL.

REGULATIONS AFTER THE ADOPTION OF THE METHOD OF REFINING BY CHLORINE, SINCE WHICH ALL SILVER OVER TWO PER CENT. IS ALLOWED FOR, ALL GOLD CONTAINING OVER TWO PER CENT. OF SILVER BEING CONSIDERED "REFINABLE."

The Treasury, New South Wales,
August 23, 1870.

REGULATIONS FOR THE RECEIPT OF GOLD FOR COINAGE AT THE SYDNEY BRANCH OF THE ROYAL MINT.

His Excellency the Governor, with the advice of the Executive Council, has been pleased to frame the following Regulations for the receipt and coinage of gold at the Sydney Branch of the Royal Mint, —such regulations to take effect from 1st September next.

1. Importations of gold-dust or gold-bullion for coinage, from 10 ounces upwards, will be receivable at the Mint daily (Saturdays and holidays excepted), between the hours of 11 A.M. and 3 P.M.

2. In addition to the charge of threepence per ounce, imposed by Her Majesty's Proclamation of the 3rd February, 1866, on the coinage of gold, there shall be paid, for melting, assaying, and refining, the following charges, viz.:—

(1.) On undivided parcels, containing not less than one thousand ounces standard (to be melted and assayed in one lot), at the rate of threepence per ounce (standard).

(2.) On parcels containing less than one thousand ounces standard, at the rate of fivepence per ounce (standard).

3. A reduction of the above Mint charges, to the amount of threepence per ounce standard, will be made in respect to gold, the produce of any other country, imported to the Mint, under the conditions prescribed in the second clause of the Act, 26 Vict., No. 5, granting a duty on gold.

4. *All silver over and above two per cent., contained in refinable gold, will be paid for at 5s. per ounce (fine).*[5]

5. The gold will be melted, if preferred, in the presence of the importer. The importer will also be furnished, on demand, with a clip for assay, from his own ingot, as a check on the Mint report.

6. Gold received up to Wednesday evening in each week will be payable on the following Tuesday. Gold received after Wednesday will be payable on the following Tuesday week.

7. The Mint will issue, if required, gold-bullion in bars or ingots, at £3 17*s.* 10½*d.* per ounce, standard. When the bars or ingots are required to be alloyed with silver, the silver will be charged for at 5*s.* per ounce.

SAUL SAMUEL.

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[5] This 2 per cent. covers every expense of refining, *i.e.* labour, fuel, chemicals, etc., and loss of gold, loss of silver, and value of silver left in the refined gold; and allows a small margin of profit varying inversely with the amount of silver contained in the original alloy operated on.

Adoption of Miller's Chlorine Process at the Mint in London.

This process was first tried at the Mint in London in 1869, with the view of toughening brittle standard gold, of which 1000 parts contain 916·6 of gold and 83·3 of copper; and the result is stated to have been quite successful. The largest quantity of standard gold subjected to this process in one operation at the Mint is 40,000 ozs., the loss on which it is asserted did not exceed 4 parts in 10,000.

In order to test the efficacy of this process, 301 ozs. of standard gold were purposely rendered brittle by the addition of 1·5 per cent. of metallic impurity, composed as follows:—Antimony 0·3, lead 0·2, zinc 0·2, iron 0·2, tin 0·2, arsenic 0·3, and bismuth 0·1. This very impure gold was melted and a stream of chlorine passed through it during 18 minutes, after which it was poured into an ingot-mould. The ingot was found to be perfectly malleable, although the metal before this treatment was "so friable that portions could readily be detached from it by the fingers."

The gold operated upon was lent to the Mint by Messrs. Johnson, Matthey, and Company, and the metals constituting the impurity were, I am informed, added in one lump to the gold when it was melted; but as the gold after having been thus rendered impure was not analysed, there is no certainty that the metals added were wholly absorbed and retained by the gold, notwithstanding that the addition was made with the greatest care by my friend Mr. Sellon, a member of the firm above mentioned. Indeed, it is probable that such was not the fact, particularly in the case of the antimony, zinc, and arsenic. The trial at the Mint was conducted by Mr. W. C. Roberts, Chemist to that establishment; and his inference from it is, that as the "brittle gold, generally met with, seldom contains more deleterious metal than $\frac{1}{1000}$ of the mass," this experiment was "sufficient to put the process to a conclusive test."

SEPARATION OF SILVER FROM GOLD BY NITRIC ACID, OR, IN TECHNICAL LANGUAGE, PARTING BY NITRIC ACID.

If Geber, the Arabian chemist, be the discoverer of nitric acid, as is generally admitted, there is reason to suppose that the method of separating silver from gold by that acid may have been known to him; for, in a treatise ascribed to him, it is stated that nitric acid (*aqua dissolutiva*) dissolves silver, and, *after* the addition of chloride of ammonium, also dissolves gold. The passage containing this statement is as follows: "Fit [aqua dissolutiva] autem multò acutior, si cum ea dissolveris quartam salis ammoniaci, quia solvit solem, sulphur et argentum."[6] [But its power is much increased by the addition of a fourth part of sal-ammoniac, as it then dissolves gold, silver, and sulphur.] It is hardly necessary to remark that silver

[6] Geber: De Inventione Veritatis, cap. xxiii. Artis Chemicæ Principes, Avicenna atque Geber, hoc Volumine Continentur. Basileæ, 1572, p. 734.

would in this case be converted into chloride, and *not be dissolved* in the present sense of that word. That Geber was, however, acquainted with a true solution of nitrate of silver is shown by his description of the process of dissolving silver, and obtaining the salt in crystals by evaporating the solution and afterwards leaving it in a "cold place."[7]

It should be added that the authenticity of the above-mentioned treatise has been questioned by Beckmann, though, according to Hoefer, "without any plausible reasons being given." The oldest account of nitric acid which Beckmann was able to find is that of Geber; but it is contained in a Latin translation, and he does not believe that such translations belong to a Geber of the eighth or ninth century, though he thinks it probable they may be of the twelfth, because "about that period aquafortis and various arts are oftener mentioned, and in a much clearer manner, in these writings."[8] It seems to me exceedingly probable that in not a few cases the credit of discoveries or inventions has been attributed to the authors of chemical treatises simply because they were the first to publish an account of them: and that many inventions had been practised long before any description of them was given to the world.

Albertus Magnus, in the thirteenth century, after describing a method of preparing nitric acid, mentions the fact that it may be used for separating silver from gold: thus he writes, "illa aqua lunam dissolvit, aurum ab argento separat."[9] Previously to 1433 nitric acid was used at Goslar for separating silver from gold.[1] Early in the following century, Paracelsus, who died in 1541, æt. 48, gave a detailed account of this process: the gold, he states, will settle like a black sand; and the dissolved silver may be recovered by immersing in the solution a plate of copper.[2]

According to Beckmann, "it appears to be an old tradition that this acid was first employed at Venice, by some Germans, for separating the noble metals, and conveyed thence as an article of merchandise to every part of Europe. The persons who prepared it were there narrowly watched, in order that the process might not become known. They were employed chiefly for separating the gold from the Spanish silver, and by these means acquired great riches. Hence arose the report that the people of Venice understood the art of making gold; and it is certain that in many countries the gold refiners were for a long time considered as gold makers; but in no period were there more gold makers than in that when separation in the wet way became known."[3]

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[7] Opus antea cit. p. 732, cap. xxi.

[8] A History of Inventions and Discoveries. By John Beckmann. Translated from the German, by William Johnston. 2nd ed. London, 1814. 4. p. 575.

[9] Theatrum Chemicum, Præcipuos Selectorum Auctorum Tractatus de Chemiæ et Lapidis Philosophici antiquitate, veritate, juro, præstantia, et operationibus, continens. Argentorati, 1613. 4. p. 938.

[1] Hoefer's Historie de la Chimie, 1842. 1. p. 469.

[2] Idem, 1843. 2. p. 19.

[3] Op. cit. 4. p. 578.

A minute and thoroughly practical description of parting by nitric id on the small as well as large scale is given by Biringuccio in his markable work, which has been previously quoted in this volume, id which was published at Venice in 1540; and the mode of pre- aring nitric acid suitable for the purpose is also described by him ith equal minuteness.[4] It is a description which may be read by odern metallurgists with interest; and if it were not so long, I ould be tempted to present a translation of it *in extenso*. A full count of the process in question is contained in Agricola's treatise De Re Metallicâ," which, however, was not published until 1556; hat is, 16 years after the volume of Biringuccio quoted above.[5]

Gulielmus Budæus, in his treatise entitled "De Asse et partibus jus," gives an interesting account of the first application of the process in Paris. On this subject I present the following extract from Beckmann's History of Inventions:[6]—"William Budæus (Budé), who was born in 1467, and died in 1540, speaks of it in his book, printed for the first time in 1516 [in the British Museum there is a copy printed at Paris in 1514], as a thing entirely new at that period.[7] A man of low extraction, named Le Cointe, first undertook to separate gold from silver at Paris, by means of a water which Budé calls *aqua chrysulca*. It is very remarkable, that by means of this water he could separate the smallest particle of gold from silver, and from every other metal; nay, he could even take from vessels their gilding without altering their form. By this act he acquired great wealth; and Budé says that both were inherited by his son, who, at the time he wrote, was the only gold refiner in Paris. He adds, that the art was exceedingly dangerous as well as unhealthy, and required great precaution. The possessor of it, when he became rich, left the execution of the work to a servant, whom he directed at a distance, that he might not expose himself to the pernicious fumes of the effervescing liquor. . . . Budé relates also, that the gold was left behind undissolved. The silver only was dissolved, and, by another art, was separated from the water [*i.e.* the solution] and

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[4] De la Pirotechnia. Lib. iii. cap. i. ii. iii. iiii. v.

[5] Hoefer, in his Histoire de la Chimie (2. p. 44), states that Agricola's treatise *De Re Metallicâ* "appeared for the first time, printed in Latin, at Basle, in 1546." But this statement is, doubtless, erroneous, as will appear from the following information on the subject, for which I am indebted to Mr. George Bullen, in the department of the Library of the British Museum. "The earliest copy of this work in the Museum Library is dated Basileæ 1556 'mense Martis.' Brunet gives 1555, 1556, and it is possible that some of the earliest copies of the edition were issued in the former year, the type being kept standing, and the later ones issued in 1556. In addition to the date being given '1556' by F. A. Schmid in his translation of 'Bermannus' [another work by Agricola], Becher in his Life of Agricola, published at Freiberg in 1819, under the title 'Die Mineralogen, Georg. Agricola . . . . und A. G. Werner,' says, 'Diese mineralogischen Pandecten erschienen, erst ein jahr nach seinem Tode, Basel, bei Froben, 1556;' and in the following page, after quoting the title at length, gives the imprint 'Basileæ apud H. Frobenium et Nic. Episcopium, MI LVI. mense Martis.' This corresponds with the Museum copy mentioned above. The date of Agricola's death is Nov. 21, 1555."

[6] Antea cit. 4. pp. 579 et seq.

[7] De Asse. Basileæ, 1556, fol. lib. iii. p. 101. Beckmann in a note gives a long extract in the original Latin.

washed. It may here be easily perceived that Le Cointe employed aquafortis; but if he was able to loosen the gold from gilt vessels without destroying them, he must have used aqua-regia, which consequently was not then unknown."

As Savot suggests, Budé believed or rather pretended that the operation was dangerous "in order to increase the profit of it;" and he adds that Budé's statement respecting the novelty of this mode of parting is confirmed "by a decree of the king, Francis I., given at Blois the 19th of March, 1540, by which article the wages of the assayers of the Mint were doubled."[8]

"From other information it appears," Beckmann states, "that the Mint at Paris purchased the art from Le Cointe's son, but still kept it a secret. On this account Francis I. (by the decree above mentioned) authorized the raising the value of coin, in order to defray the expense of fuel and assaying-water. In the middle of the seventeenth century, the preparation of aquafortis and the process of assaying in the wet way were fully known in France. At any rate, in the month of January 1637, the distillers obtained a guild letter, in which aquafortis is mentioned among the articles sold by them."[9]

But long before the time of Le Cointe, a method of separating silver and gold from each other seems to have been practised in Paris, as may be inferred from the following extract given by Beckmann:—"Dominique Honeste, Genois, obtint le 18 Sept. 1403 des lettres, portant permission de former un établissement à Paris, pour départir les matières d'or et d'argent, ce qui induiroit à croire que la découverte de ce procédé remonte au-delà du quinzième siècle, époque à laquelle les auteurs de l'Encyclopédie l'ont fixée, ainsi que celle des acides minéraux, qu'ils attribuent aux Vénitiens."[1] I agree, however, with Beckmann in thinking that separation in the wet way is not here meant, and that the question can only be decided by an examination of the original patent.

I am unable to state when the art of parting by nitric acid, either for assaying or for operations on the large scale, was first practised in England. Supposing that the archives of the Goldsmiths' Company might contain information on the subject, I requested my friend Mr. George Matthey, a prominent member of that ancient corporation, to enquire whether such was the case, a request with which he courteously and promptly complied. The result is that, according to Mr. Walter Prideaux, the clerk of the Company, the first mention of the purchase of nitric acid in their account books is in the year 1773. This statement is remarkable, because parting by nitric acid was certainly in use amongst private English assayers long before that date. Thus, Gabriel Plattes gives a short account of the process in a treatise published 1639,[2] and in another treatise by the same author,

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[8] Les Anciens Minéralogistes du Royaume de France. Par M. Gobet. Paris, 1779. 2nd part, p. 848.

[9] Opus antea cit. 4. p. 581.

[1] Almanach des monnoies. Année 1786, 12mo, p. 180.

[2] A Discovery of Subterraneall Treasure. London, 1639. p. 34.

lated 1594, this "arte of refining," as it is termed, is declared to be "of a *puisne* [*i.e.* recent] *date.*"[3] It is to be hoped that the Goldsmiths' Company will follow the example of some of the other guilds of the City of London, and record their history in a splendidly printed volume worthy alike of their reputation and their wealth; and, should they do so, I venture to suggest for their consideration the expediency of preparing as complete an account as possible of the origin and development in this kingdom of those special metallurgical operations in the practice of which many of their members were engaged at the date of their incorporation by royal charter.

The chemical reactions which occur in parting by nitric acid on the large as well as the small scale are the same, and the general course of proceeding is also substantially the same in both cases, the only difference between the two being the scale of operation. Hence much of what is stated concerning this method of parting in the article on Assaying in this volume applies equally to the processes of parting on the large scale now to be described.

Formerly nitric acid was extensively used for separating silver from gold, but in 1802 D'Arcet introduced the method of parting by sulphuric acid, which is now very largely practised throughout the world, and is specially suitable for the treatment of a great quantity of bullion at a time. For comparatively small operations, however, nitric acid is preferable to sulphuric, because it does not, like the latter, require an extensive and costly plant; but, notwithstanding the general adoption of the sulphuric acid process for large operations, the Government of the United States so recently as 1875 decided that nitric acid should be used instead of sulphuric for parting at the Mint of San Francisco. It should be stated that this decision was arrived at not because the nitric acid process was believed to be superior to the sulphuric acid process, but solely on account of the structural difficulty of providing suitable fume-condensing chambers of lead for the latter in the Mint where it was originally intended to introduce this process.[4] It affords me great pleasure to be able here to present a complete description of the nitric acid process as it is now conducted at the San Francisco Mint, and to acknowledge my deep obligation to the Honourable H. R. Linderman, Director of the Mint of the United States, for having most courteously complied with my request to be favoured with such a description for publication in this volume. And I may add that I have at all times received most willing and valuable assistance from the metallurgists of that great Republic in the preparation not only of this but of other volumes which I have published.

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[3] The *Jewell House of Art* and Nature. London, 1594. p. 79.

[4] Annual Report of the Director of the Mint to the Secretary of the Treasury for the fiscal year ended June 30, 1875. Washington: Government Printing Office, 1875. p. 84.

PARTING BY NITRIC ACID AS PRACTISED AT THE UNITED STATES MINT, SAN FRANCISCO, CALIFORNIA.

The description is given nearly verbatim, with additions (within brackets) extracted from a Report to Dr. Linderman, signed E. R. Rogers, which is contained in the Report mentioned in footnote [4] in the preceding page. It was Mr. Rogers who designed this refinery.

UNITED STATES MINT, SAN FRANCISCO, CALIFORNIA.

Melter and Refiner's Office,
January 27th, 1878.

HON. H. L. DODGE, Superintendent.

SIR,—I have the honour to acknowledge the receipt through you of two letters, one from the Honourable H. R. Linderman, Director of the Mint of the United States, dated Washington, January 15th, 1878, and one from Dr. John Percy, Lecturer on Metallurgy at the School of Mines at London, England, dated January 1st, 1878.

Dr. Percy requests to be informed as to the details of the process of parting and refining gold and silver at the Mint of the United States at San Francisco, the various appliances used, and the interior arrangements of our Refinery.

In compliance with the instructions of Dr. Linderman, directing me to furnish the information desired by Dr. Percy, I respectfully submit for your transmission to Dr. Linderman the following statement:—

PROCESS OF PARTING GOLD AND SILVER.

The exact proportions of gold and silver in a given quantity to be operated upon, having been previously determined by assay, the quantity is then made up in the proportions of one part of gold to two parts of silver.

The metal is next melted and granulated. The granulations are formed by pouring the melted metal from a dipper, in a thin stream, with a sort of wavy or circular motion, into a large copper tank, filled with cold water.

The metal is poured by hand, and the dipper is held about three feet above the surface of the water.

This action breaks up and separates the metal into small beads and shells, which are called granulations.

The granulations are then placed in large porcelain (earthenware?) jars, one hundred and thirty pounds avoirdupois weight to each jar. The jars are arranged in the corroding house, or bath. Nitric acid is then added in proportions of one and a half pound of acid to one pound of granulations. The acid has a strength of 38° Baumé.

The porcelain jars in the corroding house are partly immersed in hot water [in rectangular lead-lined troughs]. The water is kept at a boiling heat by means of a series of perforated [copper] pipes,

through which hot steam is constantly injected. The pipes are so arranged that all the water in the lower part of the corroding house, surrounding the jars, is easily affected by the steam.

About five hours usually suffice to digest the metal, after which pure water is added in order to prevent the crystallization of the nitrate of silver, and the contents are allowed to settle over-night.

On the next morning the nitrate of silver solution is drawn off, and treated as hereafter described. Two gold siphons are used to draw off the nitrate. The gold is then washed with pure water and allowed to settle, say two or three hours, and the weak solution of nitrate of silver remaining in the jars is siphoned off.

REFINING THE GOLD.

The gold is now taken from the porcelain jars and emptied into a filtering tub, and washed with hot water until every trace of nitrate of silver, or nearly every trace, disappears.

The foregoing operations altogether require two days.

On the morning of the third day the gold is placed in iron kettles and boiled twice with sulphuric acid, 60° Baumé. [In order "to expedite the process and secure greater fineness, and at the same time economize acid," Mr. Rogers introduced this modification of the usual method of parting by nitric acid.]

One hundred and fifteen pounds is the charge for each kettle. The first boiling takes about 4 hours, the second boiling about 3 hours. For both boilings two pounds of acid are used for each pound of gold; one-half of the acid at each boiling. The acid solution of sulphate of silver, after each boiling, is removed or laded off with an iron ladle.

After the boiling the gold is emptied into a common wooden double-bottomed filtering tub and washed with hot water.

While the hot water is being added, the gold is kept constantly agitated.

The gold is then allowed to settle, after which the solution is drawn off with an india-rubber siphon. This operation is repeated. The last part of the solution is drawn off by decantation. Although the gold is now nearly, or quite, pure, it is again filtered and washed until every trace of sulphate disappears.

The gold is now ready to be pressed. From 65 to 70 pounds are placed in the receiver of the hydraulic press, subjected to a pressure of 80 tons, and formed into a round cake in the form of a cheese. The pressed cakes are placed in heavy cast-iron pans, put into the drying furnace, and subjected to a strong wood-fire heat until all the moisture is expelled.

The cakes are then broken into convenient fragments for the melting crucibles, melted and made into fine bars, of which the assay fineness is from 993 to 998 thousandths. It is now ready to be made into ingots [suitable for rolling into fillets.—J. P.].

SILVER REFINING.

The nitrate of silver (drawn off as previously described) is drawn off into wooden tubs and taken to the precipitating room, and emptied into large wooden tanks. Salt water is introduced, and the chloride of silver formed is kept in constant agitation by means of a wooden agitator propelled by steam. [This arrangement consists, for each precipitating tank, of a vertical revolving shaft, carrying a cross-arm with a number of vertical blades, which dip nearly to the bottom of the tank, and which, in their circular movement, give violent agitation to the contents. The motion of the shaft is made reversible.]

After precipitation, the chloride [while under constant stirring] is drawn out [by stop-cocks] into large filters. Each filter has a capacity of 500 pounds. The chloride is then thoroughly washed with hot water. This process of washing the chloride usually occupies about ten hours.

The chloride is then removed to lead-lined reducing vats, and reduced by sulphuric acid and zinc. The proportions for reducing the chloride are as follow:—

Chloride, containing of metallic silver	420 pounds.
Zinc	140 „
Sulphuric acid, 69° Baumé	210 „

[When the reduction is ascertained to be complete, a small amount of sulphuric acid is thrown in, with a view to remove any metallic zinc that may have been left.] Water is added, and the contents are allowed to settle over-night.

On the next morning the silver is removed to circular lead-lined filters, and filtered until all traces of acid disappear. It is now nearly or quite pure, and is pressed, dried, and melted into bars, the same as gold. The assay fineness is from 998 to 999$\frac{5}{10}$th thousandths. [The average fineness of the gold received from the refinery in 1875 was 991 per 1000; and of the silver, 998 per 1000.]

DORE SILVER.

Doré silver, instead of being granulated, is melted and run into thin slabs of the following dimensions:—

Thickness	$\frac{3}{4}$ of an inch.
Width	9 inches.
Length	15 inches.

These thin slabs are placed in the porcelain jars in the corrodi house, and digested in the same manner as the process described f parting gold and silver.

APPLIANCES USED.

Copper granulating tanks.—These tanks are 2$\frac{1}{2}$ feet deep by 2 fe 8 inches in diameter.

Porcelain jars.—They are as nearly uniform in size as possible. Th dimensions are 2 feet deep and 22 inches in diameter, slightly flarin [*i.e.* widening] at the top.

Corroding houses.—There are 2 large and 4 small houses. The ge houses are 28 feet long, 5½ feet wide, and 11½ feet high, h having a capacity for 20 jars. The smaller houses are feet long, of the same width and height as the large houses, th a capacity each for 12 jars. All the houses are lined with d on the bottom, and also on the sides up to a height of 20 inches. ove the lead-lined portion the sides and ends are provided with ding doors about 4 feet long, fitted like window frames, so as to de up. The end doors are partly of glass, so that the operations hen the metal is being digested may be inspected. The tops of the uses are covered. At the centre of each house is a large fume pipe, connected with the main chimney of the Mint as to carry off the id fumes. [To prevent the escape of the fumes into the apart- ent, each pot is covered with a stone-ware lid, and the whole series closed in woodwork with sliding doors, the whole arrangement eing termed the "corroding house." Usually the nitrous fumes are llowed to pass into the chimney and to escape into the open air, and abundant may prove of serious annoyance. To correct this evil, Ir. Rogers constructed a furnace for burning coke in the attic above ie room containing the corroding houses, into which the acid fumes re conveyed and burned. It is an interesting chemical fact that these mes, so far from extinguishing the fuel, promote the combustion.]

The wooden carrying tubs are circular in form. Each tub is 8 inches deep and 18 inches in diameter.

The large precipitating tanks or tubs are raised on a platform about feet high. Each tank is 6 feet deep, 8½ feet in diameter at the op, and 10 feet in diameter at the bottom.

The chloride filters are 2¼ feet deep, 2¼ feet in diameter at the top, nd 2 feet in diameter at the bottom.

The reducing vats for silver are each 5 feet long, 2 feet deep, and ½ feet wide. The inside corners are slightly rounded.

The filtering tubs are 21 inches deep and 21 inches in diameter.

Gold boiling kettles.—Each iron kettle has a depth at the centre f 14 inches and a diameter at the top of 2 feet. The bottoms are ightly oval. The kettle, when charged, is set into the opening of a ast-iron furnace; each furnace has a depth of 3½ feet, is 2 feet high, nd 3½ feet wide. Closely covering the kettle during the boiling is lead hood, having a connecting lead pipe at the top, about 6 inches diameter, for carrying the fumes, that would otherwise fill the om, to the main chimney of the Mint.

Receiving pans.—These pans for holding the metal in the hydraulic ress are heavy cast-iron, each 12½ inches in diameter and 4½ inches eep.

All the wooden vats, tanks, filters, and carrying tubs are made of ie best wood, from 1½ inch to 2 inches thick.

Very respectfully,

(Signed) ALEX. MARTIN,
Melter and Refiner.

AMOUNT OF GOLD REFINED.

[In September 1875, 99,133·82 ozs. of gold and 528,692·08 ozs. of silver were refined; and in October of the same year, 73,168·41 ozs. of gold and 786,423·54 ozs. of silver.]

COST OF REFINING.

[The cost of refining in October 1875 was $16,000, or about 1·8 cent per ounce.]

PARTING BY NITRIC ACID AS PRACTISED BY MESSRS. JOHNSON MATTHEY, AND COMPANY, HATTON GARDEN, LONDON.

I have pleasure in acknowledging my obligation to my friends, the members of the firm above mentioned, for the following particulars as well as the drawings of their nitric acid parting refinery from which the accompanying woodcut (fig. 70) has been prepared.

The gold to be suitable for direct parting by nitric acid should not, in addition to silver, contain any other metal except palladium, copper, and lead; and the two latter metals must not be present in large proportion. If it contain tin, arsenic, or antimony, or too much copper and lead, it must be previously cupelled with lead, or refined by fusion with a flux, of which an oxidizing substance, such as nitre, is an ingredient. The gold, after having been thus purified when necessary, is melted in a plumbago crucible with the addition of sufficient silver of good quality as will produce an alloy in which the relation in weight between the gold and the silver is as 1 : 3. If auriferous silver or "Doré" be obtainable, it is, for an obvious reason, substituted for silver free from gold in preparing that alloy. The alloy is next granulated, care being taken so to conduct this operation as to prevent the formation of lumps.

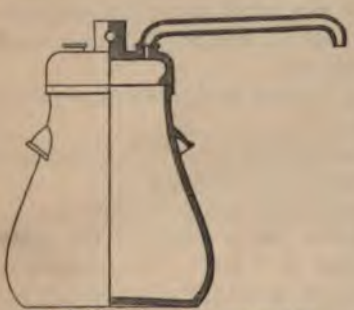

Fig. 69. Earthenware vessel used by Messrs. Johnson, Matthey, and Co. for parting by nitric acid. Drawn from the original in my possession.

It is shown half in section to the scale of 1" to 1'. It has a lug on each side to serve as a handle. The mouth is ground perfectly flat, as is also the cover. There are two holes in the cover, one on the left for pouring in the acid, and the other on the right, to which is adapted an earthenware tube for carrying off the nitrous fumes: in the centre is a vertical projecting piece, with a hole through it, so that by means of an iron rod passed through the hole it may be conveniently lifted off while hot. The tube communicates with a large earthenware pipe common to a series of parting vessels arranged on each side. This pipe is slightly inclined, so that any acid liquor carried over may be collected in a vessel in connection with the lower end of the pipe, the upper end passing into a chimney. Each parting vessel is set over a sand-bath of its own. The firm above mentioned use also large cylindrical earthenware vessels for parting, each placed in a circular movable sand-bath, and surrounded by a movable sheet of iron, of which the ends are free, the object of which sheet being the protection of the vessel from the cooling effect of currents of air. The above description of the condensing arrangement differs from that now in existence, which is shown in fig. 70.

The granulated metal is heated with nitric acid in vessels of white earthenware or of platinum. The earthenware vessels are either cylindrical or of the form shown in fig. 69. Each vessel is provided

with a well-fitting cover, also of earthenware, having an opening from which, by means of a tube of the same material, the nitrous fumes produced in the process pass through a condensing arrangement such as is shown in fig. 70. This arrangement is necessary in order, as far as practicable, to intercept and collect the minute particles of acid liquor, containing nitrate of silver in solution, which are projected into the upper part of the porcelain vessel during the effervescence accompanying the action of the acid on the alloy, and which would otherwise escape along with the fumes. The uncondensable part of the fumes is conveyed into the ashpit of the furnace *g*, in which the gold is melted, whence it passes upwards through the fire, so that the nuisance, which would otherwise result from the escape of these fumes into the atmosphere, is effectually prevented.

The form of the platinum vessel used and manufactured by Messrs. Johnson, Matthey, and Company is shown in fig. 70. It is of the capacity of about 9 gallons, weighs approximately 300 troy ounces, and costs about £450. The cover is of earthenware, to which is adjusted a tube of the same material, connected with the condensing arrangement previously mentioned. Each vessel is heated by a separate furnace, of which a vertical section is shown in fig. 70, the fuel being either gas-coke or coal-gas from a series of jets.

The charge of granulated metal for a single platinum vessel of the dimensions stated is 800 ozs., and it is boiled three times successively with fresh nitric acid, of the same strength, *i.e.* nitric acid of sp. gr. 1·4, diluted with its own volume of water free from chlorine. In the first operation 50 pints of acid are added, and kept gently boiling for 4 hours, by which treatment the greater part of the silver is dissolved. The acid liquor is poured off, and the residue boiled for 3 hours with 30 pints of fresh acid; and in the third and last operation of the same kind 20 pints of fresh acid are added and the boiling continued during only 2 hours. In this final boiling so little silver is removed that the acid may always be used over again in a first boiling of the granulated metal.

After the last boiling with nitric acid, the gold is placed on large earthenware funnels with perforated bottoms, and washed with boiling distilled water until the intermixed solution of nitrate of silver is, as far as possible, removed; but in order to separate this solution completely, it is necessary further to wash the gold in large dishes of porcelain or earthenware, or of platinum, with boiling distilled water, and at the same time stir well with a spatula of platinum or porcelain.

The washed gold is dried, melted in plumbago crucibles, and cast into bars, which weigh about 200 ozs. troy each. When the process has been properly conducted, the gold will be 998 fine, *i.e.* will not contain more than 2 parts alloy (in this case silver) in 1000 parts. In parting by nitric acid alone on the large scale it is not practicable to obtain the gold absolutely free from silver; and the degree of purity above stated is considered sufficient for all ordinary commercial purposes.

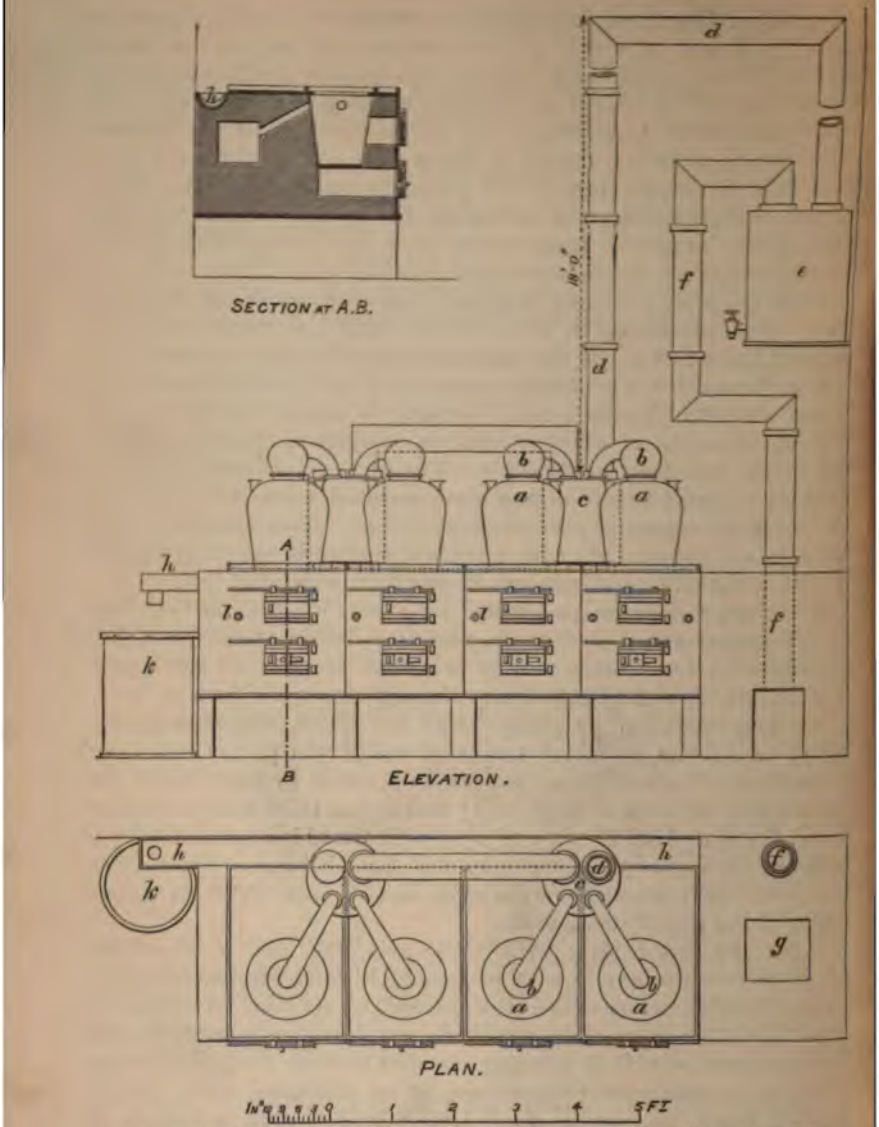

Fig. 70. Parting by nitric acid in platinum vessels, with the arrangement for carrying off the nitrous fumes.

a, *a*. Platinum vessels, each provided with two tubulated openings for pouring in the acid. *b*, *b*. Covers of earthenware, to each of which is adapted a tube of the same material for carrying off the nitrous fumes. The ends of the tube fit into water joints. *c*. Earthenware receiver, connected with a pair of the vessels *a*, *a*, by means of the tubes fitted to the covers *b*, *b*. *d*, *d*. Earthenware pipe. *e*. Earthenware receiver, in which acid liquor not condensed in *c* is collected. *f*, *f*. Earthenware pipe, which descends and communicates with the ash-pit of a melting furnace. *g*. Melting furnace. *h*. Gutter for catching acid liquor in the event of overflow or breakage. *k*. Vessel to receive any acid liquor from *h*.

Each platinum vessel is set over a separate fireplace, of which the construction is shown in the section at A.B. From the back of the fireplace near the top descends a narrow circular flue into the main flue communicating with the chimney; and from each side also near the top descends a similar flue into a horizontal flue *l*, which communicates with the main flue; and by this arrangement particles of fuel and ash carried downwards may be easily removed by means of a scraper introduced through *l*, *l*, at the front.

By operating in the manner described with ten platinum vessels of the dimensions stated, and of which four are shown in fig. 70, 2000 ozs. of gold can be refined per day of 12 hours, by one head-refiner, two assistants, and a melter.

The silver contained in the solution and washings is precipitated as chloride by the addition of common salt; the chloride of silver, after having been well washed with boiling water, is subjected to the action of granulated zinc and water acidulated with sulphuric acid; and the silver, so reduced to the metallic state, is washed, dried, melted, and cast into bars, which are about 998 fine.

In 1837, my respected friend the late Mr. Percival Norton Johnson, at that time head of the firm in Hatton Garden, informed a Select Committee of the House of Commons on the Royal Mint, that their charge for parting gold was 7 shillings per lb. troy, returning the alloy whether consisting wholly of silver, or of silver and palladium.[1] Before the same Committee, Mr. Mathison, an official of the Mint designated "Master's first clerk, melter, and refiner," stated that for refining (*i.e.* in this case parting by *sulphuric* acid) gold for coinage, "when it was necessary to bring the metal up to the standard" he charged the Mint 6¾*d.* per oz., or 6*s.* 9*d.* per lb., and 1*d.* per oz. for silver, or 1*s.* per lb.[2] The process was conducted at the Mint with platinum vessels, etc., paid for out of the public purse, Mr. Mathison having no salary and contracting to do the work at a price agreed upon between the Master of the Mint and himself. Certain expenses, such as those for materials and labour, were defrayed by himself, and his remuneration consisted of the profit which he could make by this work. But he was also permitted to refine at the Mint for the Bank of England and for private individuals, and in that case his charge was only 2*s.* 3*d.* per lb. on gold and 8*d.* per lb. on silver.[3] That Mr. Mathison derived considerable profit from the contract in question is probable from the fact that, whereas Messrs. Johnson and Company charged 7*s.* per lb. for parting with nitric acid, which is much dearer than sulphuric, Mr. Mathison charged the Mint only 3*d.* per lb. less than that firm, notwithstanding he carried on his operations with the cheaper acid and in a refinery erected and provided with costly apparatus at the national expense![4]

A somewhat startling admission was made by Mr. Mathison in his evidence before the Select Committee of the House of Commons, as will be seen in the following questions and answers:—

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[1] Report from the Select Committee on the Royal Mint; together with Minutes of Evidence, Appendix and Index. *Ordered, by* The House of Commons, *to be Printed*, 30 *June* 1837. p. 162. Questions 2293 and 2294. This Report contains much highly interesting and valuable information.

[2] Idem, p. 113. Question 1729.

[3] Idem, p. 113. Question 1730. But out of these sums Mr. Mathison paid to the Master of the Mint 3*d.* for every lb. of fine gold, and 1*d.* for every lb. of fine silver, delivered out of the refinery, in consideration of his privilege of using the Government plant for the purpose.

[4] According to Ure, the charge of the refiners in London, who were "obliged, for fear of prosecution [for creating a nuisance?], to employ the more expensive, but more condensable, nitric acid," was 4*s.* per lb. troy. (Dictionary of Arts, Manufactures, and Mines, 1839. p. 1062.)

"Q. 1206. Were you connected with the Mint in any manner before you were appointed to the office [melter and refiner] you now [1837] fill there?—No.

"Q. 1207. Had you previously been engaged in any pursuits analogous to the duties which have devolved upon you in the melting department?—I had not."

SEPARATION OF COPPER FROM SILVER BY SULPHURIC ACID.

The problem of separating copper from an alloy of silver and copper, containing the latter in large proportion, does not appear to have been satisfactorily solved except in particular cases involving specially favourable local conditions.[5] Although it is one that may now rarely present itself, owing to the introduction in recent times of *wet* processes, by which silver is extracted from the regulus produced in the smelting of argentiferous copper ores, yet it may nevertheless occur, as I know from my own experience, having once been engaged in experimenting upon it on a considerable scale. For this reason it seems to me desirable to direct the attention of metallurgists to an interesting paper on the subject by Bucholz, published in 1803, which is probably not generally known. Moreover, this paper acquires additional interest from the fact, that its date is nearly coincident with that of the introduction by D'Arcet, in 1802, of the method of parting by sulphuric acid next to be described, to which Bucholz makes no allusion, as it is fair to infer he would have done if he had heard of that method. The title of the paper of Bucholz is as follows:—"Researches with a view to discover a cheap and short method of separating copper and silver from each other, or rather to prepare silver free from the copper, with which it is alloyed or otherwise mixed, instituted by Christian Frederick Bucholz, and communicated along with other not unimportant experiments made on the same occasion."[6]

Bucholz states that when his researches were undertaken, the only liquid reagent in use for the separation of silver and copper from each other was nitric acid, when it occurred to him that possibly sulphuric acid might be advantageously substituted for that acid on account of its much lower price. He consulted chemical books[7] on the action of sulphuric acid on silver and copper in the metallic state; but not finding in them such information as seemed to favour his notion, he determined to experiment upon

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[5] In large gold and silver parting establishments the problem has been solved by melting silver alloyed with much copper with a due proportion of silver free from copper, or containing only a small quantity of it. But there are many localities in which such large establishments do not exist.

[6] Versuche zur Ausfindigmachung eines wohlfeilen und abgekürzten Verfahrens, Kupfer und Silber von einander abzuscheiden, oder vielmehr um das Silber rein von dem Kupfer, womit es legirt oder sonst vermischt ist, darzustellen: angestellt und nebstandern bey dieser Gelegenheit gemachten, mit nicht unwichtigen Erfahrungen mitgetheilt; von Christian Friedrich Bucholz. Neues allgemeines Journal der Chemie. Berlin, 1803. 1. pp. 149–173.

[7] "Chemische Lehr- und Handbücher."

he subject himself. He soon found that his books were untrustworthy guides, and it is amusing to note how on one occasion he xults over them. "To my delight," says he, "this result also was very lifferent from the statements in chemical books."[8] The knowledge f this little incident may possibly not be useless to chemists of the resent day, if it should awaken in their minds wholesome doubt as to he truth of many of the so-called facts, which have been perpetuated, nquestioned, by one generation of writers on chemistry after another or centuries past; and for that reason I have inserted it here.

Bucholz has recorded the results of twenty experiments, several f which are worth notice.

I. One dram of pure silver was boiled in a little retort, with a eceiver attached, with $\frac{1}{2}$ oz. of pure nitrate of potash, 2 drams of oncentrated sulphuric acid, and 2 drams of water. What passed over as put back into the retort, and the mixture was heated again. After the lapse of $\frac{1}{4}$ hour, $\frac{2}{3}$ of the silver were found to be converted nto sulphate and dissolved.

II. The experiment was repeated during $\frac{1}{2}$ hour with 1 dram of ilver, 1 oz. of nitrate of potash, 5 drams of concentrated sulphuric cid, and $\frac{1}{2}$ oz. of water. The silver was wholly converted into sulphate and dissolved. The solution was diluted with 8 ozs. of distilled water and heated to the boiling-point, when 2 loths of copper oin were put into it. In $\frac{1}{4}$ hour the sulphate of silver was very asily decomposed by the copper, and the silver separated in the metallic state; and on afterwards filtering and crystallizing the liquor, a "rhombic" salt of a light verdigris-green colour was obtained in pretty large quantity, which behaved like "cupriferous sulphate of potash." In the residual liquor there was still much free acid.

The large quantity of nitrate of potash required in the preceding experiments to effect the solution of silver convinced Bucholz of the unprofitableness of such a method of separating silver from copper, even without regard to the fact that copper would require for its solution three times as much oxygen as silver, and, therefore, three times as much nitrate of potash. He made similar experiments with nitric acid, and came to the same conclusion with respect to it; after which he experimented on the solvent action of sulphuric acid.

III. Two loths (= 8 drams) of copper filings were heated with 4 loths of sulphuric acid, of sp. gr. 1·896. As soon as the mixture had become thoroughly heated, sulphurous acid was evolved, but ceased after the lapse of about an hour. The temperature was then raised until the sulphuric acid began to evaporate, yet without causing any further evolution of sulphurous acid. As there remained very much sulphuric acid upon the saline mass which had formed, the whole was kept at a boiling temperature for 4 hours. After cooling, there was still left much extremely concentrated acid; but it was found that only 1 dram and 2 scruples of copper had been dis-

[8] "Zu meiner Freude war also auch das Resultat dieses Versuchs sehr verschieden von den Angaben der chemischen Lehrbücher," p. 165.

solved out of the 8 drams operated upon. The experiment was repeated with 2 loths of copper filings and 6 loths of concentrated sulphuric acid, when 2 drams and 1 scruple of the former were dissolved. In another experiment 1 loth of copper filings was kept in 3 loths of boiling sulphuric acid, of the same density, for 18 hours, a long-necked flask being used for the purpose; and afterwards, the excess of sulphuric acid which remained was driven off. Sulphurous acid was only evolved at first, as in the preceding experiments; and not more than exactly 70 grains of copper were dissolved, or a little over $\frac{1}{4}$ of the weight of the copper operated upon.

IV. Copper was heated to the boiling-point with sulphuric acid more or less diluted, and found to be vigorously attacked, sulphurous acid being all the while copiously evolved. A saline mass was formed, which, when moist, was grey-green, but whitish-grey when thoroughly dried, and which, on the addition of water, dissolved, with the exception of a small quantity of copper that had not been acted upon. A mixture consisting, by weight, of 2 parts of concentrated sulphuric acid and 1 part of water was shown to be the best for dissolving copper; and these are the proportions which Berzelius prescribed for converting metallic copper into sulphate by the direct action of sulphuric acid at the temperature of ebullition.[9] Bucholz supposed that water might act by yielding oxygen to the copper, in which case hydrogen would be set free; but this supposition was negatived by the fact that the sulphurous acid evolved contained not a trace of hydrogen. The gas was passed into water, when a little sulphur, which seemed to have been produced at the commencement of the experiment, was observed in the water. Another supposition was that the water might act by supplying the requisite quantity of water of crystallization to the sulphate of copper formed, and this Bucholz considered to be the most probable. It was not, in his opinion, the salt with which the copper became coated in the foregoing experiments which prevented the further action of the sulphuric acid, because, after that coating was removed, the action was not renewed [a statement opposed to modern experience.—J. P.].

V. Silver was found to dissolve completely, with the aid of heat, in a little less than its own weight of concentrated sulphuric acid, and the sulphate of silver formed readily dissolved when a sufficient quantity of water was added. Bucholz then shows that the cost of dissolving copper and silver in nitric acid is much greater than in sulphuric, and asks, who would not prefer the method of separation by sulphuric acid, apart even from the consideration that the cost of this acid would probably be defrayed by the sale of the sulphate of copper produced, whereas the recovery of the nitric acid from the nitrate solution generally requires long processes?

VI. Bucholz operated upon alloys of silver and copper in his three concluding experiments, but I insert only the following account of

[9] Traité de Chimie. Paris, 1847. 4. p. 158.

ıe last. Two pounds of silver coin, containing different proportions f alloy, but of an average fineness of 10-16ths (*zehnlöthig*, i.e. 10 loths ɔ the mark of 16 loths or 8 ounces), were cut into pieces as small as racticable. Although this quantity of the metal required, according ɔ computation, only $3\frac{1}{2}$ lbs. of concentrated sulphuric acid, yet, with a iew to quicken and increase the action, he used 3 lbs. 10 ozs. of acid nd $1\frac{1}{2}$ lb. of water. The mixture of metal and acid was strongly eated in a glass vessel on a sand-bath as long as sulphurous acid ontinued to be evolved, the mass being frequently stirred with a lass rod. To the dry, whitish, greenish-grey saline mass 8 lbs. of istilled water were added, and the whole kept at a boiling heat ntil the mass was dissolved. The silver was thrown down from he solution by metallic copper; and in order to preserve the silver rom admixture with particles of copper, reduction was effected by ieans of 1 lb. of copper coins, placed loosely in a coarse linen bag, hich was suspended in the solution. Gentle heat was applied, and ept up for two hours, when the whole of the silver was found to be recipitated. The supernatant liquid was poured off, and the precipi-ıte washed with distilled water as long as ammonia acted upon it. he silver, after having being washed, dried, and heated to low red-ess, weighed 1 lb. 10 loths. The solution containing the sulphate f copper was evaporated in a copper vessel to the "crystallization-oint," and after several crystallizations $4\frac{1}{2}$ lbs. of "beautifully crys-ıllized sulphate of copper" were obtained. The residual mother-quor contained much free sulphuric acid and some copper.

"Thus," writes Bucholz, "the result of these various experiments, specially the latter, has confirmed our hopes, which the action of ulphuric acid on copper and silver, when separate, led us to enter-ain, and we have discovered a new method of parting cupriferous ilver (*Zerlegungsmethode*), corresponding to our wishes, as it is cheaper han those heretofore in use, and is, at the same time, easily racticable. I need scarcely mention, that in the event of the silver till retaining a trace of adherent copper salt, the finishing touch to ts purification may be given by digesting it with a little weak ammonia; or if the silver should not be in an incoherent state, the same result may be attained by melting it with $\frac{1}{3}$ or $\frac{1}{4}$ of its weight of pure nitrate of potash."

Bucholz gives a summary of his conclusions, from which I extract the following:—

I. Ordinary concentrated sulphuric acid, of 1·896–1·900 sp. gr., does not dissolve even so much as $\frac{1}{100}$ part of the weight of the copper in spite of long digestion at a boiling heat.

II. The more concentrated the sulphuric acid is, or becomes, during the operation, the more does its action decrease.

III. A certain degree of dilution with water promotes and quickens the action of the acid to such a degree, that not the twentieth part of the time and heating, and only $3\frac{3}{8}$ parts of the acid, are required to render soluble 1 part of copper.

IV. Concentrated sulphuric acid dissolves somewhat more than its own weight of fine silver, and without requiring any dilution with water.

V. Silver may be perfectly separated from its admixture with copper by means of sulphuric acid diluted to the degree indicated in these experiments.

NOTE ON THE BLACK SUBSTANCE FORMED BY THE ACTION OF SULPHURIC ACID ON COPPER UNDER CERTAIN CONDITIONS.

It has been long known that during the solution of copper in heated sulphuric acid a black powder is formed, which at first was considered to be cuprous sulphide. Maumené, however, who investigated this subject, asserts that, under certain conditions, a compound of equal equivalents of that sulphide and cupric oxide is also produced. But, according to Spencer Pickering, who has recently made very numerous experiments on the same subject, the results of which he has communicated to the Chemical Society of London, the statement of Maumené is inaccurate; and the conclusions at which he has arrived are as follow:—During the solution of pure electrotype copper in pure strong sulphuric acid, of sp. gr. 1·843, at a temperature below 270° C., a certain quantity of cuprous sulphide is formed along with anhydrous cupric sulphate. The proportion of cupric sulphide is in the inverse ratio of the temperature, and at or above 270° C. any cupric sulphide which may have been formed is decomposed, being converted into anhydrous cupric sulphate with the liberation of sulphurous acid. The cuprous sulphide appears as a black coating upon the metallic copper, and retards the solvent action of the sulphuric acid upon the latter. The rate at which copper is dissolved increases with the concentration of the acid (?) and the temperature. During the treating of copper with strong sulphuric acid at 100° C., this rate increases rapidly at first, but after reaching a maximum begins to decrease, owing chiefly to the protective action of the coating of sulphide, and also to the increasing diminution in the density of the acid. At the temperature of 100° C. commercial sheet copper has been found to dissolve in pure strong sulphuric acid at a much greater rate than pure electrotype copper. (Journal of the Chemical Society, 1878. 33. pp. 112 and 139.)

SEPARATION OF SILVER FROM GOLD, OR PARTING, BY SULPHURIC ACID.

Hoefer, in his History of Chemistry, claims for Kunckel, who lived in the 17th century, the merit of having originated the method of separating silver from gold by sulphuric acid. The passage which contains this claim is as follows:—

"*Emploi de l'huile de vitriol pour séparer l'argent de l'or.* Ce procédé, qui est considéré par quelques chimistes comme une découverte récente, était également connu de Kunckel, qui dit: 'L'huile de vitriol dissout l'argent, mais seulement en faisant bouillir la liqueur;

cette même huile de vitriol ne dissout pas l'or, qui peut être ainsi séparé de l'argent.'"[1]

In order to test the accuracy of this quotation, the same edition of Kunckel's treatise as that in which it is stated by Hoefer to occur[2] has been very carefully examined at my request by my friend Mr. Hochstätter Godfrey, and the passages which he has found relating to this subject, literally translated, are the following:—

Any one desirous of dissolving it [silver] in oil of vitriol should take silver either in the shape of beaten-out leaves or filings, or as precipitated by copper, pour upon it twice its weight of oil of vitriol, namely 2 loths of oil for each loth of silver, and put the vessel containing the whole on a sand-bath which can be heated by a strong fire. After the fire has been burning slowly for a while, it is increased, when the oil begins to boil with the formation of bubbles. As soon as these bubbles have passed away the solution or liquid flows like water and looks as clear as crystal (p. 287). . . . . When a hot acid solution of sulphate of silver is poured into cold oil of vitriol, the sulphate is precipitated (p. 294). . . . . It is stated that oil of vitriol does not dissolve gold (pp. 163, 202, 253).

Particular search was made in the volume in question for the inference from the facts above mentioned, which, as given by Hoefer, in his extract between inverted commas, would indicate that Kunckel had actually proposed the use of sulphuric acid for parting silver from gold. That inference is contained in the words "[l'or] qui peut être ainsi séparé de l'argent;" but no words to this effect occur in the original.

Scheffer, in 1753, communicated to the Royal Swedish Academy of Sciences a paper on the "History of Parting," in which he states that strong sulphuric acid, with the aid of heat, might be used instead of nitric acid for separating silver from gold; though it could not be profitably employed for that purpose, because it was much more costly than nitric acid.[3] Scheffer also mentions the fact that this strong acid dissolves tin, and considers that by its means tin may be most accurately separated from gold, care being taken to remove all the sulphate of tin formed before washing the gold with water, which would precipitate any sulphate of tin that might be present.

To C. D'Arcet is ascribed the merit of having been the first to part silver from gold on the large scale by means of sulphuric acid; and a refinery on this principle was erected in Paris in 1802, according to his designs.[4] But it appears that Dizé before that date, while

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[1] Histoire de la Chimie, 1843. 2. p. 211. The first volume was published in 1842. The work from which this extract is stated to have been obtained is Kunckel's "Vollständiges Laboratorium," 4th edition, 1767. p. 288 (see foot-note in Hoefer's treatise, v. 2. p. 201).

[2] Vollstaendiges Laboratorium Chymicum. Vierte verbesserte Auflage. Berlin, 1767.

[3] Historie vom Scheiden von H. Th. Scheffer. Abhandlungen der Königl. Schwedischen Akademie der Wissenschaften, 1753. 15. p. 7. Published in 1756.

[4] This C. D'Arcet was nephew of Jean Pierre Joseph D'Arcet, member of the Institute of France, who held the office of "Inspecteur Général des Essais des Monnaies." See "Seconde Instruc-

D'Arcet was employed as his assistant, when he held the office of "Affineur National des Monnoies," suggested the use of sulphuric acid for separating the traces of silver left in gold parted by nitric acid; and directed D'Arcet to experiment on the subject. D'Arcet obeyed this direction, and found that on boiling the gold with sulphuric acid, of the strength indicated by 66° of Baumé's areometer (= sp. gr. 1·815), the silver which it had retained was extracted.

The process of parting by sulphuric acid was adopted at the Mint in London in 1829, and was introduced by Mr. Mathison, at that time melter and refiner there.[5] The manner in which Mr. Mathison procured information on the subject deserves a notice, and is recorded in the following extracts from a Report prepared and communicated September 28, 1831, by that gentleman himself to Lord Auckland, then Master of the Mint.[6]

"He [the late Master of the Mint, Mr. Herries] observed that the Mint had been established at a great expense for a great national object, viz. that of insuring to the public the most perfect coinage and the most effectual perpetuation of it which Government could direct, and whilst in all mechanical parts we stood confessedly superior to any similar establishment [which cannot now be said—J. P.], it seemed to him not only inconsistent but discreditable that the refining branch, with which I had the honour to be more immediately connected, was as remarkably behindhand with the course of improvement in other countries. He urged me, therefore, in the strongest manner, to acquire by every means in my power the necessary information, so as to render any and every service connected with my department which could be executed in other countries. The result of my first enquiries was very disheartening; I could hear of no English chemist who was acquainted with the process in question, and no English refiner had ever practised it; no description of it had ever been published [which is not correct, as a full account of it had been published by D'Arcet (the uncle of C. D'Arcet) in 1827]. In Paris, the secret (for such it was considered) lay among few persons, and no precautions were spared to prevent it becoming known, especially to Englishmen. I was about to proceed to Paris, when an accidental circumstance facilitated my enquiries. A French attorney called at the Mint, and left a written statement in the hands of Mr. Morrison on this very subject. Mr. Morrison referred him to me, and I ascertained that one of the persons who had been employed in a French refinery,

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tion relative à l'Art de l'Affinage; redigée par M. D'Arcet." Paris, 1828. p. 6. This paper was written by the uncle, J. P. J. D'Arcet. Dizé published a letter in the Journal de Physique (1802. 55. pp. 437-440), in which he complained that C. D'Arcet had claimed for himself the credit of having originated the method of subjecting gold parted by nitric acid to the action of strong boiling sulphuric acid in order to separate the silver which it retained; and asserted that this claim was wholly unfounded, as C. D'Arcet in this matter merely acted as "manipulateur" in conducting experiments which he had directed him to make. This letter was in reply to a communication to the same Journal (55. pp. 259–263) from C. D'Arcet, in which he put forth the claim in question.

[5] Report from the Select Committee on the Royal Mint, antea cit., p. 117, Question 1783.

[6] Idem, Appendix A, p. 59.

recently established in the Kent Road, and who had been discharged in the ordinary course of business, was solicitous of employment in the Mint.[7] I readily availed myself of his services, with Mr. Herries's sanction, and the results of the experiments, which we made together on a very small scale, emboldened me to believe, that if tried on a larger scale, the result would prove equally satisfactory. To do this, however, it was necessary for me to incur an expense of at least £1000; and as I had no certain knowledge or experience to direct me, I perceived the difficulty of obtaining money for what must be termed experimental purposes. . . . Just at this time some of the parties concerned in the French refinery already alluded to, called upon me, and represented in strong terms the risk which would be run." In part of the answer to Question 1783, "Have you made any improvement in your mode of refining since 1829?" Mr. Mathison says, "When I began in 1829, I began, from the necessity of the case, without any experience at all; I bought every particle of experience I possess."[8]

It would be interesting to know how much the French attorney received for the information which he imparted to Mr. Mathison; but not a word is stated on that point.

In 1846 and 1847 being engaged in experiments on a somewhat large scale on parting by sulphuric acid, I called upon Mr. Mathison at the Mint, in the hope of being permitted to inspect the process of parting by sulphuric acid then in operation there, as I had the impression that it was a Government establishment and there were no secrets to conceal. I need hardly add that I was refused admittance. If I had known that this establishment was virtually a private one, though erected at the national expense, I should not have applied for permission to witness its mysteries.

The process of refining at the Mint was abandoned in 1851, and in 1852 the refinery there was leased to the late Sir Anthony Rothschild, and is now in the occupation of a member of the Rothschild family. Another large sulphuric acid parting establishment was erected at Limehouse, near London, by Mr. Henry Lewis Raphael about 1865, and continues in operation; and there is also a third of the same kind, belonging to Messrs. Johnson, Matthey, and Company. I have visited the first and last of these refineries.

Parting by sulphuric acid is now largely practised both in Europe and America, and even at the new Japanese Mint at Osaka.

When the process of parting by sulphuric acid was first carried out on the large scale, the solution of the metal alloyed with the gold was effected in cast-iron vessels; but these were soon afterwards replaced

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[7] The late Dr. Ure states that the refinery on the French system of parting by sulphuric acid was erected by M. Costell in Pomeroy Street, Old Kent Road; but he was not successful in his enterprise, and after he had relinquished the business the same system was introduced into the Royal Mint, under the management of M. Costell's French operatives. A Dictionary of Arts, Manufactures, and Mines. By Andrew Ure, M.D. London, 1839. p. 1059.

[8] Report antea cit. p. 117.

by vessels of platinum. It is, however, singular, that for many years vessels of cast-iron have been generally substituted for those of platinum, and are now very extensively used. According to Dumas, the credit of re-introducing cast-iron vessels is due to M. Tocchi of Marseilles.[9]

DESCRIPTION OF THE PROCESS OF PARTING BY SULPHURIC ACID.

For the following elaborate description I am indebted to Dr. Heinrich Rössler, of Frankfort-on-Main, who has been engaged during many years in conducting parting on a large scale by this method. The description was written in 1870, but has been revised by Dr. Rössler in 1878.

The process of parting by sulphuric acid will be described under two general headings, viz.:—

I. Parting of auriferous silver.

II. Parting of argentiferous gold.

Introductory Observations.—This method of parting is founded on the fact that boiling concentrated sulphuric acid dissolves silver, but has no action on gold, which subsides to the bottom of the vessel in which the operation is conducted. Simple as this method of parting appears, it is often rendered difficult owing to the admixture of other metals, and the behaviour of the salts which are produced from them. The action of sulphuric acid upon various metals will be briefly considered, *seriatim*:—

Silver.—Pure metallic silver readily dissolves in boiling sulphuric acid of 66° B. (*i.e.* Baumé's areometer), with the liberation of sulphurous acid, and the formation of a clear, colourless solution, which consists of sulphate of silver dissolved in excess of concentrated sulphuric acid. Boiling concentrated sulphuric acid dissolves sulphate of silver in all proportions; and even when this salt is heated to the boiling-point with $\frac{1}{4}$ of its weight of the acid, a clear solution is produced, which on cooling becomes a mass of white crystals. But cold concentrated sulphuric acid dissolves only $\frac{1}{4}$ its weight of sulphate of silver. To convert 1 equivalent of silver into sulphate, 2 equivalents of sulphuric acid are theoretically required; so that with 9 parts by weight of boiling concentrated sulphuric acid, 10 parts of silver may be converted into sulphate, which will remain dissolved in the excess of acid. [See p. 43, antea; but in the reaction there stated water does not appear. As, however, hydrated sulphuric acid must be used to form sulphate of silver, water is set free during the solution of the silver; and that is a point to be borne in mind. The reaction is as follows:—

$$Ag + 2(SO^3, HO) = AgO, SO^3 + SO^2 + 2HO.$$
$$[2Ag + 2(SO^3, H^2O) = Ag^2O, SO^3 + SO^2 + 2H^2O.]]$$

[9] Traité de Chimie appliquée aux Arts. Paris, 1833. 4. p. 466.

In dissolving on the large scale, from 2 to 2½ parts of sulphuric acid are usually employed for 1 part of silver, as the solution when it is poured off, though still hot, is no longer at the boiling temperature. The colder the solution becomes, the larger is the quantity of sulphate of silver which separates and forms a deposit on the bottom of the vessel. When the solution of sulphate of silver is poured into water, the greater part of this salt is precipitated as a white powder. One part of sulphate of silver requires for solution—

180	parts of	cold water.		
88	„	boiling water.		
180	„	cold sulphuric acid	of	10° B.
30	„	boiling „	„	10° B.
20	„	„ „	„	20° B.
4	„	cold „	„	66° B.
¼	part of	boiling „	„	66° B.
55	parts of	„ neutral solution of sulphate of copper		of 10° B.
45	„	„ „ „	„	„ 20° B.
35	„	„ acid „	„	„ 10° B.

Gold.—Pure metallic gold, as previously stated, is not attacked by concentrated *pure* sulphuric acid; but as neither protoxide nor peroxide of gold is insoluble in sulphuric acid, in the event of the formation of these compounds, loss of gold is quite conceivable.

Protoxide of gold is formed when gold is boiled in sulphuric acid containing nitric acid, and is precipitated when the resulting yellow solution is diluted.

Peroxide of gold is formed when chloride of gold is decomposed by nitrate or sulphate of silver.

As both oxides are decomposed, with the precipitation of metallic gold, by prolonged boiling with sulphuric acid of the highest degree of concentration, no loss of gold is to be apprehended when sulphuric acid containing nitric acid or chlorine is used. To what extent the other metals may be separated from gold by boiling sulphuric acid will be hereafter considered under the head of "Parting of Argentiferous Gold."

Platinum and Palladium.—In parting a platiniferous alloy by sulphuric acid no platinum is dissolved, as is the case in parting by nitric acid: the platinum remains with the gold. But it is sensibly attacked when boiled for a considerable time with sulphuric acid of the highest degree of concentration; and so is palladium, even to a still greater extent. In the presence of much silver both of these metals seem to be unattacked, because, owing to the continued liberation of water during the solution, sulphuric acid of the highest degree of concentration can never be present.

Copper.—This metal, when alloyed with silver, is wholly converted into sulphate by boiling concentrated sulphuric acid; but since its chemical equivalent is only about ½ of that of silver, three times as much sulphuric acid is required for the formation of the sulphate, as in the case of silver; so that the larger the proportion of copper in an alloy, the more must the quantity of sulphuric acid be increased. In practice, the quantities of sulphuric acid usually employed to

dissolve coppery alloys of silver containing different proportions of silver are as follow:—

950	per 1000	of silver,	2	parts	of sulphuric acid.
900	"	"	2½	"	"
875	"	"	2¾	"	"
750	"	"	3	"	"
600	"	"	3½	"	"
and to dissolve 1 part of unalloyed copper			4	"	"

Sulphate of copper dissolves only in small quantity in boiling sulphuric acid, to which it imparts a beautiful bluish-green colour, which disappears on cooling, the copper salt being nearly wholly precipitated. The great mass of the sulphate of copper formed is left undissolved as a white anhydrous salt, which, along with the gold and a portion of sulphate of silver, settles to the bottom. When this salt is produced in large partings of silver not of a very high standard (*nicht ganz hochhaltigem Silber*), it is usually not white but brown, owing partly to an admixture of other metals, partly to organic matter adherent to the alloy operated upon, and partly to graphite from the cast-iron vessels. Very coppery alloys are more difficult to dissolve than those of a high content of silver, owing to the formation of anhydrous sulphate of copper, which, being insoluble in sulphuric acid, encrusts the pieces of alloy under treatment and stops the further action of the acid, unless this evil is prevented by constantly stirring and routing up (*stochern*) the mass. Copper itself can only be converted into sulphate, when it is finely divided, the larger particles remaining undissolved. If the residue is thrown into water, the whole of the copper-salt is dissolved out in the state of blue-vitriol; but it must be thrown in gradually, for, if not, lumps of the anhydrous salt are formed which only slowly dissolve.

Lead.—Metallic lead alone cannot be easily converted into the sulphate by boiling sulphuric acid, especially because at this temperature it softens and cakes together; but it can be more easily oxidized when it is alloyed with silver. As sulphate of lead is only slightly soluble in boiling, and still less soluble in cold, sulphuric acid, it subsides, and forms a sediment on the bottom. The separation of sulphate of lead during the gradual cooling of the solution of plumbiferous silver, frequently imparts a turbid milkiness to the solution. On pouring this milky solution into water, the sulphate of lead is entirely precipitated.

Tin.—This metal, like silver, dissolves in concentrated sulphuric acid, and forms a clear colourless liquid, from which, when poured into water, a white basic salt is precipitated. In dissolving an alloy containing gold and tin in sulphuric acid, a kind of purple is always formed, which occasionally imparts a deep-red colour to the residue, consisting of sulphates of copper, lead, etc. In parting alloys of gold and silver containing tin, sulphate of tin is formed, and the gold residue, as well as the silver precipitated from the solution, contains some tin.

Zinc.—This metal is oxidized by sulphuric acid with difficulty; or which reason brass is less easily converted into sulphates than opper alone. Sulphate of zinc is insoluble in sulphuric acid, and it emains therefore with the copper in the residue, from which it may e dissolved out by water.

Iron.—Iron is only attacked very gradually by sulphuric acid of 6° B.; whence the possibility of using iron pots for parting. A mall quantity of iron is, however, always converted into anhydrous ulphate of protoxide of iron, which, being entirely insoluble in the oncentrated acid used, remains along with the copper in the residue. Occasionally the silver solution is rendered turbid; owing to its eing quite full of small scales of this salt in a state of suspension. Experience has shown that iron pots are much less attacked by ulphuric acid when the alloy under treatment contains a consider- ble amount of copper. Grey pig-iron is much more attacked by he acid than white pig-iron; and in pots made of the former the olution may appear filled throughout with small scales of graphite letached by the solvent action of the acid upon the cast-iron. Sesqui- xide of iron dissolves in considerable quantity in concentrated ulphuric acid, and colours it yellow.

[According to Levol, the following equation expresses the reaction when iron is acted upon by hot concentrated sulphuric acid (Chem. Gaz., 1851. 9. p. 5, quoted from the Journ. de Pharm., Nov. 1850):—

$$Fe^2 + 6(SO^3,HO) = Fe^2O^3,3SO^3 + 3SO^2 + 6HO.$$

$$[Fe^2 + 6(SO^3,H^2O) = Fe^2O^3,3SO^3 + 3SO^2 + 6H^2O.]$$

We find, as Rössler states, that ferrous, not ferric, sulphate is formed under these conditions.—J. P.]

PRESENCE OF GOLD IN ARGENTIFEROUS ORES AND SILVER COINAGE.—All the silver as yielded by ores is more or less auriferous. Silver from pure lead ores contains the least gold; while that from pyritic ores, especially such as contain copper, antimony, and arsenic, is frequently rich in gold.

By means of sulphuric acid, from 0·03 to 0·05 per cent. of gold can be extracted from silver with advantage; whereas by the older and expensive methods, silver containing 0·08 per cent. of gold could not be parted with profit, this being the average amount of gold found in silver coin of an earlier date than 1830, and in the silver from lead-smelting works.

PARTING OF AURIFEROUS SILVER.

The method now in use at most of the larger parting establishments in which varieties of auriferous silver, inclusive of "Blicksilber" from the smelting works, are treated, consists of the following operations:—

I. Dissolving out the silver in cast-iron vessels.

II. Pouring the sulphuric acid solution into water, and precipitating the metallic silver by copper with the aid of steam.

III. Washing the residue and obtaining the gold.

IV. Washing, pressing, heating, and melting the silver.
V. Manufacture of sulphate of copper, from the solution from which the silver has been precipitated.

I. Dissolving out the silver.—After the commencement of parting by sulphuric acid, platinum vessels were used, but they have now nearly everywhere been displaced by those of cast-iron. In a few of the smaller establishments, as at Oker, in the Harz Mountains, porcelain vessels are still in use. All iron vessels must naturally become much worn in the course of time, and a parting vessel cannot, with safety, be kept in constant use longer than 2 years.

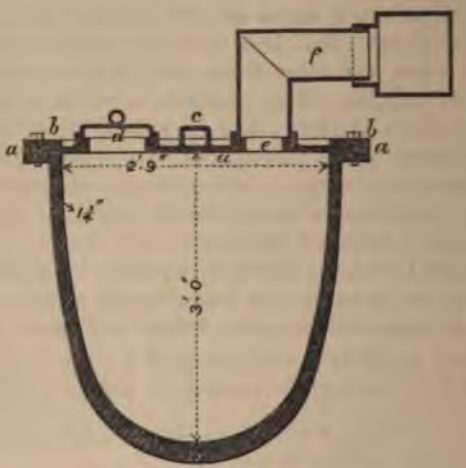

Fig. 71. Parting pot of cast-iron.

a. The cover of the pot. b. Cast-iron ring.
c. Bearer of wood placed crosswise, for strengthening the cover. The sectional shading has been omitted.
d. Opening through which the metal and acid are introduced, and the solution is laded out.
e. Opening to which is adapted a bent leaden pipe *f* for carrying off the vapours.

In the accompanying woodcut, fig. 71, is shown a cast-iron pot, suitable for treating from 200 to 250 kilogrammes of alloy at one time. The cover of the pot is made of thick sheet lead, and is supported by a piece of wood *c*, or bearer, placed crosswise on the top, to which it is attached by strips of sheet-lead soldered on. It is kept in its place by a cast-iron ring *b*, screwed to the rim of the pot. There are two openings in the cover, of which each is provided with double vertical projecting rims, so as to form an annular gutter: one for introducing the alloy, the acid, and an iron spatula for stirring, for observing the progress of the operation, and for lading out the solution at the end of the process; the other, to which is fitted a bent pipe *f* for the escape of the vapours, which pass through a pipe into leaden conduits (*bleierne Kanäle*), and thence to a chimney with a good draught. Most of the sulphuric acid which evaporates is collected in those conduits, together with small particles of sulphate of silver, which are mechanically carried over from the pot.

am jets are used to promote and regulate the draught through conduits. In some parting establishments, as at Vienna, the den conduits are connected with leaden chambers, in which the aping sulphurous acid is reconverted into sulphuric acid.[1]

The charge for a pot varies from 100 to 500 kilogrammes, accord- to the manner of working. Only about 5 hours are required to solve from 200 to 250 kilogrammes of granulated fine silver; but m 8 to 10 hours are required to dissolve completely the same antity of bars or other kinds of silver of 875 or 900 fine. About f the requisite quantity of acid is added at first, and cautiously ated to the boiling-point; effervescence then commences, and be- nes very violent when the silver is in a granulated state. After it s begun to boil care must be taken so to regulate the temperature to prevent the liquor from boiling over, which is particularly t to occur when granulated metal is treated. The workman ust continually watch the boiling, and prevent too vigorous action adding cold sulphuric acid, which should be kept at hand for the rpose. Towards the end of the process recourse is had to stirring th an iron spatula, in order to free the still undissolved pieces of oy from the surrounding sediment, and expose them to the action the boiling acid: the stirring is continued as long as any pieces of oy can be felt with the spatula. During the stirring the remainder the sulphuric acid, calculated from the fineness of the alloy to be cessary, is gradually added. In the case of alloys rich in copper, nstant stirring is essential, in order to prevent the formation of mps of anhydrous sulphate of copper, which would adhere to the ttom of the pot, and lessen or prevent contact between the acid and e granulated metal.

After the dissolving is completed, the liquor is left to cool for ne time, generally during the night, in order that the suspended e particles of gold may settle down, and the solution become cool ough to be laded out without injury to the workmen. The deposit, ich consists of the sulphates of silver, lead, and iron (protoxide), l contains all the gold, should, on the following morning, be found the state of a firm sediment on the bottom of the pot and sharply arated from the solution, which should now be perfectly clear. e colour of the solution from alloys of high standand is generally ht green, but brownish from alloys of low standard. Sometimes solution remains turbid and milky, which might raise a suspicion t particles of gold had been removed along with the liquor; but s turbidity may be owing to various causes, namely, the separation rystals of sulphate of silver when the liquor is too much cooled,— en to the presence of lead in the alloy treated,—and most frequently sulphate of protoxide of iron, resulting from the action of the acid

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[1] Glauber appears to have been the t to use leaden cisterns for the conden- on of acid vapours. Three cisterns his kind which he had in his labora- contained 1040 lbs. of sheet-lead. The Works of the Highly Experienced and Famous Chymist, John Rudolph Glauber. Translated into English by Christopher Packe. London, 1689, p. 418. —[J. P.]

on the sides of the pot, and which, being insoluble in concentrated sulphuric acid, remains suspended in the liquor. To ensure obtaining a clear solution under all circumstances, a special clarifying process has been introduced in many parting works. This consists in adding to the hot solution, some time before it is removed, from 3 to 4 litres of cold sulphuric acid of 52° B.: by thus diluting and cooling the solution at the surface, crystals of sulphate of silver separate, which fall quickly to the bottom of the pot, and carry with them all particles held in suspension, such as sulphates of lead and iron, and fine particles of gold. When treating coppery alloys, the solution clarifies easily, as the sulphate of copper dissolved by the boiling sulphuric acid separates on cooling, and carries down all particles suspended in the solution as it falls to the bottom; and, consequently, in parting such alloys no fear need be entertained that fine particles of gold will be removed along with the liquor. Besides, the anhydrous sulphate of copper adheres strongly to the bottom of the pot, so that the solution can be completely poured off. For this reason, in the treatment of silver of very high standard, some coppery alloy is frequently added in order to collect the gold in a larger quantity of sediment and so keep it firmly at the bottom of the pot. Besides, when copper is present the sides of the pot are far less attacked, and, consequently, less sulphate of protoxide of iron is separated.

In some of the largest English and French parting establishments, the whole of the turbid liquor is drawn off from the dissolving pot, by means of a platinum siphon, into a large leaden cistern containing acid liquor or water, and the whole is boiled until the sulphate of silver is dissolved; and as soon as the gold has subsided, the solution, while still very hot, is drawn off. The disadvantage of this method is that most of the gold which had settled down in the iron-pot is stirred up again in the silver solution; but there is this advantage, that parting can be carried on continuously, and a large quantity of alloy be dissolved in small pots.

This process is conducted in the following manner:—From about 100 to 150 kilogrammes of alloy are dissolved in the least possible quantity of acid in a small pot, the time occupied being only a few hours. The contents of the pot are then drawn off into a large vat, which contains just sufficient acid liquor to dissolve all the sulphate of silver (about 30 parts to 1 part of the salt), and immediately afterwards the pot is charged again. During this second dissolving the solution is left until it becomes clear, when it is drawn off from the residue into a vat of the same dimensions set at a lower level in which the silver is precipitated: in this manner the work can be carried on uninterruptedly. Great care is required to prevent gold from being drawn off along with the silver solution, for any gold so removed would be lost in the precipitated silver.

When treating alloys containing less than 60 per cent. of silver, the solution cannot be removed in the manner first described, as the sulphates of copper and lead are then present in too large quantity. In this case the method last described has to be employed.

II. Pouring the sulphuric acid solution into water, and precipitating the metallic silver by copper with the aid of steam.—The ar solution of the silver is baled out with copper ladles into a ugh communicating with precipitating vats; or before entering se vats, the solution is laded into small copper pots and there left settle for a short time. The precipitating vats, which are rectgular, are made of wood lined with sheet lead; and they are ovided with pipes for directly injecting steam into the solution. e vats are charged with water, or with the dilute liquors resulting m the washing of former residues; and, after the sulphate of silver lution has been run in, steam is injected until boiling occurs, and ost of the sulphate of silver which had separated when the solution me in contact with the water or liquor in the precipitation vats, as ove described, is redissolved. During this time small pieces of scrap pper are added; and the precipitation of the silver is promoted constant stirring with wooden staves. When the work is well ne, and the liquor is not stronger than from 25° to 28° B., the preipitation will be completed in 1½ hour. By using four vats, each metre high, 1 metre wide, and 1½ metre long, 200 kilogrammes of lver can be precipitated in that time. Three parts by weight of etallic silver require for precipitation about 1 part of copper. After aving been carefully tested for silver by means of common salt, to ake sure that it contains not the smallest trace of silver, the solution left at rest for two hours, and then transferred to leaden vats, so at any mechanically suspended particles of silver may be deposited.

[For some years past the silver has been precipitated from the lphate solution by scrap iron instead of metallic copper. After dilun with water, the solution of sulphate of silver is left to crystallize. he crystals obtained are removed from the acid solution, stirred up water, and scrap iron is then added gradually until every trace of lver is precipitated, while any copper that may be present remains solution, as only sufficient iron is added to precipitate the silver. he impurities separated from the scrap iron are easily slagged off hen the precipitated silver is melted, and the fineness of the resulting r silver is almost greater than that obtained by precipitation with etallic copper. The chief advantages of this method are: 1. Saving acid, as the mother-liquor from the crystals of the sulphate of lver is made use of in dissolving fresh alloy; 2. Avoiding the rchase of copper which cannot be sold advantageously in the form blue-vitriol, since the establishments at Freiberg and the Harz roduce this salt in such large quantities; 3. Economy in steam, as e sulphate of silver solution becomes very hot by the heat libeted during the solution of the iron, whereas formerly in precipiting with copper the solution had to be heated by steam; 4. The ssibility of treating large quantities of alloy in comparatively nall localities. Dr. Rössler, Annal. d. Chem., 1876. 180. p. 240.]

III. Washing the residue and obtaining the gold.—During the me occupied in boiling the silver solution in one set of vats, the sidue (which contains all the copper and gold, together with much

silver, as well as any lead that may be present) is transferred to another set of vats (*Staubgoldpfannen*), previously filled with water or dilute acid liquor if such be available. This second set of vats are of the same size and construction as the silver-precipitating vats above described, but are placed at a higher level, so that the liquor may be drawn off from them by means of a siphon into the precipitating vats. The solution is boiled by means of steam, as in the former case, while the residue is continually stirred. When this operation is finished, the solution (which should contain all the sulphate of copper and most of the sulphate of silver previously in the residue) is allowed to settle for about two hours, and is then, if clear, drawn off into a precipitating vat, ready for use in diluting the solution of sulphate of silver from the next parting. When necessary, this operation is repeated until only a small amount of sulphate of silver remains with the gold (*Staubgold*, dust-gold); this sulphate is then converted, by boiling with the addition of copper, into metallic silver, which is precipitated. After this the solution is allowed to settle, and when clear is drawn off; and the argentiferous gold is collected, washed, heated to redness, and then melted with nitre. If the original alloy contained lead, the sulphate of lead formed will remain with the gold. Sulphate of lead is not acted upon by the copper used to precipitate the silver. The sediment from the "Staubgold" vats consists of metallic silver and gold, with sulphate of lead. If this sediment is melted in clay crucibles without flux, the unchanged sulphate of lead forms a slag covering the metal; and since this slag always retains some silver, it is remelted with charcoal-powder, by which nearly the whole of the noble metals are reduced.

Fig. 72. Small deep pot of cast-iron.

Fig. 73. Porcelain dish shown in vertical section.

The form of the side on the left is intended to retain the residue during decantation of the wash-water.

It is rarely economical to produce fine gold from auriferous silver in one operation; so much time and labour would in that case be required that it is considered desirable to concentrate the gold in a small quantity of silver, which can then be alloyed with other gold which has to be parted.

The following process, however, of obtaining fine gold direct from the residue is in use at some parting establishments, as at Munich. This method is only applicable when the alloy does not contain copper

base metals in considerable quantity, and when perfectly
d is not required. The process is conducted in the following
:—The whole residue is transferred to small deep pots of
shown in fig. 72, and boiled several times with sulphuric
which treatment nearly the whole of the sulphate of copper
a small portion of the sulphate of silver are left undissolved:
can be used again for the next parting. What remains
ved is transferred to a porcelain dish, such as is shown in
section in fig. 73, and washed with boiling water, until the
s cease to give a reaction for silver. In this manner the
freed from the associated
s of silver and copper:
above stated, if nearly
fine gold be required,
be submitted to another
which will be described
quel (see p. 470).

WASHING, PRESSING, HEAT-
D MELTING THE SILVER.—
ecipitated silver, in the
a lustreless grey powder,
nto a colander made of
d coated with perforated
d, and washed with hot
ntil the washings cease
the reaction for copper,
sted by ammonia. The
tained by the silver is best
l in a hydraulic press.

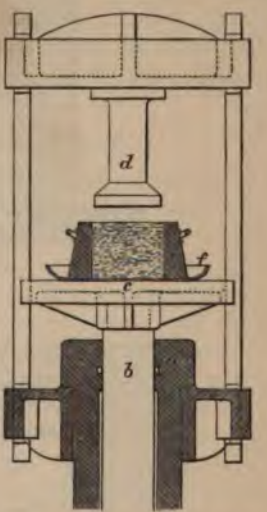


Fig. 74. Hydraulic press, not to scale.
a. Cylinder. b. Ram. c. Table.
d. Follower to the press-head.
e. Mould or box, made of cast-iron.
f. Copper-dish or receiver.
d, e, and f were formerly circular, but are now made rectangular.

cakes of pressed silver
l by heating them in the
the melting-furnaces, or
ly in a retort-furnace
ted for the purpose. In
rnace as that shown in fig. 75, p. 468, from 30 to 40 kilo-
of silver can be heated at one time, but occasional stirring
ed.

dry silver is melted in cast- or wrought-iron, or in black-lead
o obtain silver from 998 to 999 fine, care has to be taken that
particles of the scrap copper used for precipitation remain
silver; and when necessary, the silver is melted with the
of nitre, either in clay pots or in black-lead pots coated on
e with clay.

ary wind-furnaces are generally used for melting the silver,
ome parting-works furnaces with a mechanical blast are
l, and recently gas-furnaces have also been introduced.
s of the furnace communicate with a culvert, in which the

[2] *Glühen*, which literally means to glow.

silver carried off mechanically is deposited. All the old pots and the ashes of the fuel are ground up and sifted to extract the shots of metal which they may contain, and the residual fine stuff is smelted as sweep at lead-works.

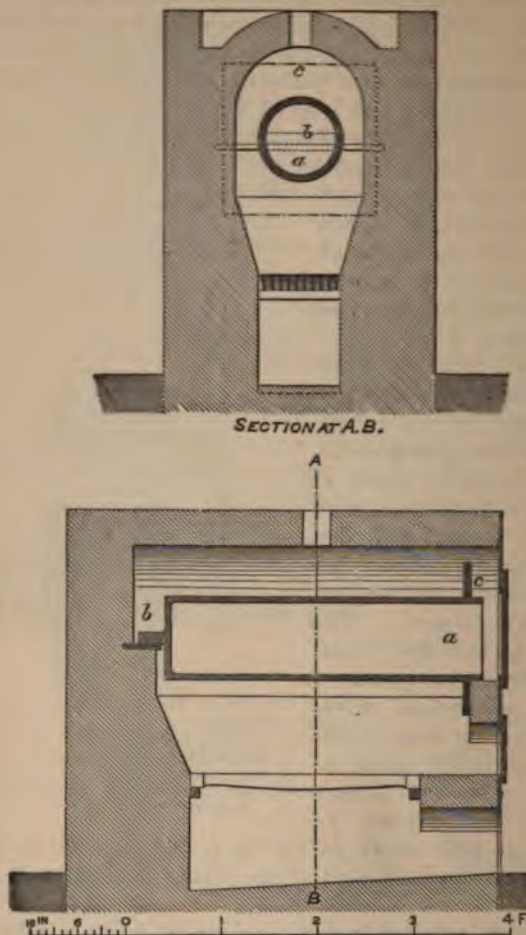


Fig. 75. Retort and furnace in which the silver, after compression, is heated.

a. Retort of cast-iron.
b. Snug cast on the closed end, by which the retort is held in position.
c. Plate of cast-iron, with a round opening, which supports the open end of the retort.

V. MANUFACTURE OF SULPHATE OF COPPER FROM THE SOLUTION FROM WHICH THE SILVER HAS BEEN PRECIPITATED.—The acid solution of sulphate of copper is from about 25° to 28° B.; after settling for a while in a vat intended for that purpose, it is transferred to evaporating tanks. It is there concentrated (the tanks being heated by means of steam coils) to from 40° to 42° B., and thence run into rectangular crystallizing vats. "Crude blue-vitriol" is thus obtained, and purified

recrystallization. The acid "mother-liquors" are further concentrated up to 60° B., in leaden vessels; whereby all the copper is adually separated in the state of anhydrous sulphate of copper the form of reddish-brown crusts, which are from time to time moved, and the colour of which is due to the presence of sesquioxide iron in combination. The acid, which thus concentrated has a ack colour from suspended organic matter, is either used for the anufacture of sulphate of iron or is further concentrated up to ;° B. in parting pots, so as to render it suitable for dissolving esh alloy. The crusts which separate from the acid liquors are dissolved, and produce, on crystallizing, an impure blue-vitriol. hen the acid mother-liquors become too much charged with iron, e copper remaining in solution is recovered by precipitation with rap iron.

PARTING OF ARGENTIFEROUS GOLD.

By parting of argentiferous gold is meant the separation of silver d base metals, such as copper, from alloys containing so large a roportion of gold as to be usually designated "gold;" or, otherwise ated, this parting is in reality a refining of impure gold.

The substances treated under this head are alloys rich in gold, ch as native gold which always contains silver (the proportion which is usually from 5 to 20 per cent., but may reach even 30 r cent.), and the bars derived from jewellers' scrap and sweep, hich, besides gold, silver, and copper, often contain lead and tin. latinum is frequently present in small quantity, as also are alladium, osmium, and iridium. Copper in small quantity is not jurious, but under no circumstances ought it to exceed 10 per cent. ot more, however, than a few thousandths of lead and tin should e present, if it is desired to obtain fine gold. Hence bars of low andard, especially such as contain lead and tin, are, previously to rting, melted in clay crucibles with the addition of nitre, in order slag off the base metals; but if the latter are present in large uantity, this fusion is attended with risk, because the crucible is so werfully corroded by the oxide of lead and cuprous oxide which e formed that perforation of it may occur. It is therefore far tter in such cases to dissolve the bars along with auriferous silver ee p. 462), to put the whole mud-like mass into the "Staubgold" ts, wash, precipitate, and melt without the addition of flux, by hich means there is obtained an alloy of gold and silver free from se metals, and suitable for parting,

The method of obtaining fine gold introduced by D'Arcet, and rfected by Pettenkofer, is now used, with slight alterations, at arly all parting establishments. It consists of the following opetions:—

I. Dissolving the silver and boiling the gold (*Auflösen des Silbers und Auskochen des Goldes*).

II. Washing the boiled gold in order to free it from copper (*Waschen des ausgekochten Goldes* [*Befreiung von Kupfer*]).

III. Heating with bisulphate of soda.
IV. Melting the gold.

I. Dissolving the silver and boiling the gold.—For this purpose small cast-iron pots are most convenient for use, which are so light that, by means of a lifting apparatus, they can be easily removed from the fire and the liquor poured out. In such a pot as is represented in the accompanying woodcut, fig. 76, about 30 lbs. of granules can be treated. The dissolving of this quantity with from 2 to 2½ times its weight of acid is completed in 2 hours' boiling. The pot is then taken from the fire, left to cool somewhat, and the solution to settle, after which it is slowly poured off into small copper vessels, in which it is again left to settle. After settling, the solution is transferred to precipitating vats; or if a large parting of silver is being carried on at the same time, it is far better to pour the solution into that of the silver in the large parting pot, because it has, in that case, a longer time for settling, and there is greater certainty of preventing loss of gold. The gold in the cooled pot has still to be boiled twice with the same weight of sulphuric acid as used in the first boiling, each time at least for an hour. This acid, as it contains only a small quantity of silver, is again used for dissolving silver.

Fig. 76. Small cast-iron pot for dissolving the silver and boiling the gold.

II. Washing the boiled gold to remove sulphate of copper.—In order to remove the copper, nearly the whole of which remains, in the state of sulphate, with the gold, the boiled mass, after the last acid has been poured off, is washed with hot water in leaden dishes. When the gold is in fine powder, great care must be taken that not too much of it floats away: all the wash-water used is collected and put into the "Staubgold" vats. The washing is continued until the wash-water is no longer bluish, and is found by testing to be free from silver.

III. Heating the gold with bisulphate of soda.—The parted gold is mixed with 25 per cent. of its weight of calcined sulphate of soda, and put into small iron-pots in quantities of from 10 to 15 lbs.; and for every 10 parts of the salt, from 6 to 6½ parts of concentrated sulphuric acid are added, to form the bisulphate. The mixture is heated till the salt becomes liquid, and stirred with an iron spatula until the excess of acid is evaporated and the gold again becomes dry. The same quantity of acid as at first is now added, and boiled until there remains only a part of the bisulphate formed, as the whole of the silver should by this time have been converted into sulphate. A larger quantity of acid is then added, and boiled in order to extract the salts; and at last the gold is washed clean with hot water in porcelain or leaden dishes.

IV. Melting the gold with nitre.—The gold from the last opera-

tion, which is spongy and brownish-red, is dried in porcelain dishes, afterwards mixed with $\frac{1}{16}$ of its weight of nitre and melted in Hessian crucibles. The resulting slags, which are full of small shots of gold and contain the platinum in an oxidized state, have to be subjected to a special process.

The gold must always be melted with nitre when it is desired to obtain it perfectly malleable. Platinum renders gold less ductile, and an admixture of 1–10,000th of lead or tin suffices to make gold brittle.

Results of Experience in Parting.

The best results in parting by sulphuric acid are obtained when the percentage of gold and copper together in the alloy does not much exceed 25 or fall much below 18 per cent. The process can, however, be practised successfully when the quantity of silver is only twice that of the gold; but in this case the boiling with sulphuric acid must be long continued, in order thoroughly to penetrate to the interior of the granules of the alloy. Although alloys containing less than 18 per cent. of gold, and even not more than 0·5 per thousand, can be parted by sulphuric acid, yet the separation of the silver from the gold becomes less complete as the proportion of silver increases. Complete separation, however, of the two metals is not possible; but whilst the residue from metal rich in gold usually contains only a few thousandths, and never above 1 per cent. of silver, the silver increases in that from metal poor in gold up to 3 or 4 per cent. According to Pettenkofer,[3] the silver, which after such long-continued boiling with sulphuric acid is retained by the gold, may be almost completely extracted by heating the latter with a fixed alkaline bisulphate. After this treatment the gold retains only a few thousandths of silver, and usually from 1 to 2–1000ths of platinum, this metal being scarcely ever absent, and sometimes being present in greater proportion than that just mentioned. This amount of platinum, according to Pettenkofer, by whom it was first pointed out, causes a sensible increase in the silver left in the gold. When, after heating with bisulphate of soda, the gold does not retain more than 4–1000ths of silver and 2–1000ths of platinum, it can, by fusion with nitre, be converted into tough gold of from 998 to 999 fine. Absolutely fine gold can only be obtained with perfect certainty from an impure alloy by dissolving in aqua-regia the gold obtained by boiling with sulphuric acid, separating the chloride of silver by filtration, and precipitating the gold from the solution by sulphate of protoxide of iron. This method is only practised in a few parting establishments; but it has the unmistakable advantage above all others of producing by careful manipulation perfectly pure gold from every kind of alloy treated in parting, and at the same time, if it be well conducted, it is neither more expensive nor more lengthy than the process of heating with bisulphate of soda or potash. Gold coin, and, generally speak-

[3] Dingler's Polyt. Journ. 104. p. 129.

ing, gold of a high standard, *i.e.* containing at most 10 per cent. of silver, is most advantageously freed from silver by dissolving it directly in aqua-regia.

FINANCIAL DETAILS.

These details are not contained in the original paper furnished to me by Dr. Rössler. In 1875 somewhat more than 200,000 kilogrammes of silver were obtained as the result of parting at the German Gold and Silver parting establishment at Frankfort-on-Main (*Deutsche Gold und Silber Scheideanstalt in Frankfurt am Main*).[4] The charge for parting amounts on the average to 1·2 mark per kilogramme (=0·44 penny per ounce troy) of alloy varying from 300 to 900 fine (*i.e.* inclusive of gold and silver). In a well-conducted establishment the loss of silver in parting ought not to exceed 0·1 per cent. of the silver contained in the alloy operated upon.

All the auriferous silver[5] produced at the smelting-works of the Oberharz is parted at the establishment attached to the Lautenthal smelting-works. During the year 1876, 22966·45 lbs. of auriferous silver (inclusive of 0·45 lb. of coin) were parted, and yielded 166·38 lbs. of gold bars containing 166·153 lbs. of fine gold, 155·11 lbs. of these gold bars being derived from foreign ores. In the preceding year only 64·7185 lbs. of gold bars were produced. The cost of parting per lb. of auriferous silver amounted to 39 pfg., and, after deducting the profit derived from the sale of the sulphate of iron obtained as a by-product, to 37 pfg. (*i.e.* 0·27 penny per ounce troy). In the preceding year the latter figure amounted to only 35 pfg. (*i.e.* 0·26 penny per ounce troy).

At the Commune smelting-works at Oker, 5069·19 lbs. of auriferous silver were parted in 1876, and furnished 25 lbs. of gold; but in the preceding year 20·24 lbs. of gold were produced. The cost of refining and parting the "blicksilber" amounted to 60·5 pfg. per lb. of "blicksilber" (*i.e.* 0·44 penny per ounce troy).

Occurrence of Platinum, Palladium, Selenium, and Bismuth in Alloys subjected to Parting.

The following information has been extracted from a paper published by Dr. Rössler in 1876:[6]—

Most of the silver obtained by cupellation appears to contain platinum and palladium, and sometimes in sufficient quantity to communicate a dark-yellow colour to its solution in nitric acid. The proportion of platinum metals in old coins appears to be pretty uniform, and the silver from Commern and Mechernich in the Eifel

[4] Annalen der Chemie, 1876. 180. p. 240.

[5] Refined "blicksilber," *i.e.* completely cupelled silver. See the Author's volume on the Metallurgy of Lead. Zeitschrift für das Berg-Hütten und Salinen Wesen im Preussischen Staate. Berlin, 1877, vol. 25, part 6 (statistical volume, 1st part), p. 199.

[6] Ueber das Vorkommen von Palladium, Platin und Selen in den Silbermünzen; von Dr. *H. Rössler*. Annalen der Chemie, 180. p. 240.

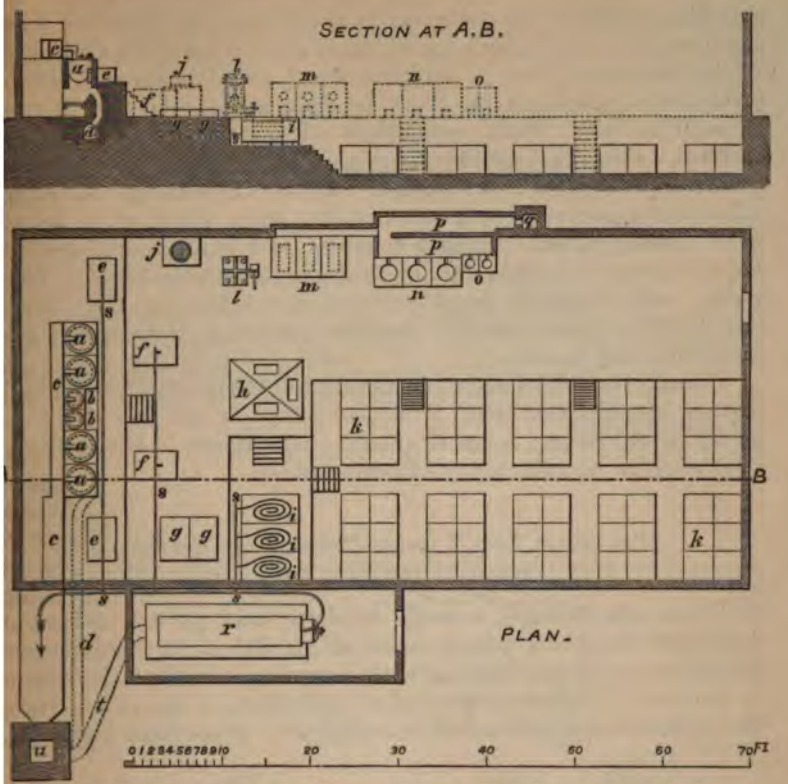


Fig. 77. The plan of a parting establishment, illustrative of the foregoing description by Dr. Rössler, and designed for the treatment daily of 1000 kilogrammes of alloy.

a, a, a. Large parting pots.
b, b. Small ditto.
c, c. Leaden conduits for carrying off the acid vapours from the parting pots.
d. Flue communicating with the fire-places under the parting pots.
e, e. "Dustgold" vats (*Staubgoldfannen*).
f, f. Silver precipitating vats.
g, g. Settling vats for the copper solution.
h. Office covered in with glass.
i, i, i. Evaporating pans for the copper solution.
j. Sieve for washing the precipitated silver.
k, k. Crystallization vats for copper solution.
l. Hydraulic press.
m. Retort furnaces for drying the precipitated silver.
n. Melting furnaces for the silver.
o. Ditto ditto gold.
p, p. Flues connecting the melting furnaces with the chimney.
q. Chimney.
r. Boiler.
s, s, s. Steampipes.
t. Flue for the boiler fire.
u. A high chimney connected with the parting and boiler fires.

mountains contains 0·0058% of platinum and 0·0053% of palladium. These two metals are obtained as by-products in manufacturing nitrate of silver, and in the preparation of fine gold by the wet way. In the first case they remain in the residue, and in the second they are precipitated as a black powder by metallic iron from the ferric chloride solution obtained in precipitating gold, dissolved in aqua-regia, by ferrous chloride. This black powder is digested with ferric chloride in order to remove the greatest part of the copper present, after which it is dissolved in aqua-regia. Any gold in the solution thus obtained is thrown down by ferrous

chloride, and then the platinum is precipitated by chloride of ammonium, and the palladium by ammonia and hydrochloric acid.

An interesting fact is the presence of selenium, as well in the precipitated gold as in the black precipitate previously mentioned. In melting this black precipitate with carbonate of soda and charcoal, a slag rich in selenium is produced, from which the selenium can be separated with advantage. Rössler in heating to redness palladium precipitates obtained a molten mass, which, when treated with aqua-regia, was partially dissolved, and hard, heavy, brilliant scales, closely resembling osmium-iridium, were left behind. These scales were found to be constituted according to the formula (Pd Pt) + Se, palladium and platinum replacing iridium, and selenium replacing osmium.[†]

Bismuth has been found in nearly all kinds of silver; but in parting by sulphuric acid, it is lost partly in the fine silver and partly in the slags. A small quantity of bismuth is obtained as a by-product in manufacturing nitrate of silver.

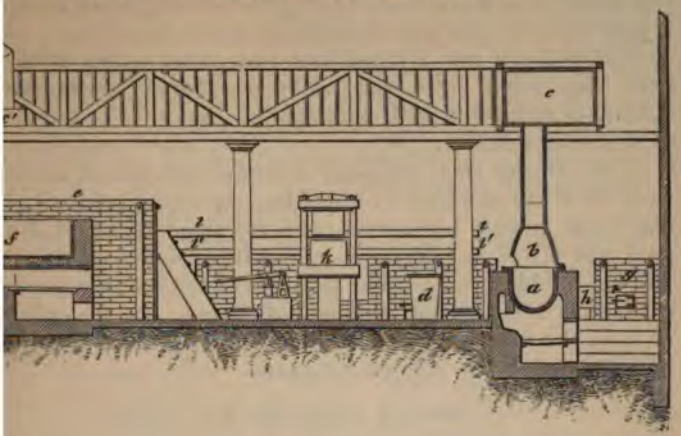
Sulphuric Acid Parting Refinery at Septêmes, near Marseilles, France.

There was formerly a small sulphuric acid parting refinery at Septêmes, under the management of M. Fabre, who published a description of it, accompanied with engravings, in the "Bulletin de la Société de l'Industrie Minérale," 1857–1858, 3. pp. 118–130; but its operations were suspended in July 1856. From those engravings

[†] In parting about 500,000 lbs. of alloy during the year 1875, 12 lbs. of platinum, 2 lbs. of palladium, and several pounds of selenium were recovered as by-products.

a, a, a, a, a. Dissolving vessels of cast-iron.
b. Cover, and pipe of lead communicating with the chamber *c*.
c. Condensing chamber of lead, set on a floor supported by cast-iron pillars.
c'. Receiver of lead, into which the sulphuric acid condensed in *c* is conveyed.
c''. Pipe, through which the uncondensable fumes pass from the receiver *c'* into the chimney *o*.
d, d, d. Vessels of lead to receive intermediately the hot solution from the dissolving vessels *a, a, a, a, a*.
e, e. Settling tanks of lead, set over sand-baths. These tanks are designated *caisses des marcs*, the word *marc* here meaning the insoluble residue of impure gold formed in dissolving the granulated metal.
f, f. Precipitating tanks, which are made of lead, and set over sand-baths: they are at a lower level than *e, e*.
g, g. Copper boiler for heating the water to be used in washing. The mark above the top of the fire-door on the left is intended to represent a stop-cock. It should also be shown in the plan in front of *g*, but has been accidentally omitted.
h. Tank for washing, the bottom of which is slightly inclined.
k. Hydraulic press.
l, l. Trough of wood, lined with lead, to convey the coppery solutions to that part of the refinery where these solutions are treated; the communication between the two parts of the refinery is effected by means of a movable trough crossing the court-yard which separates these parts from each other.
l', l'. Trough of wood, lined with lead, by which the mother-liquors and acids are returned from that part of the refinery where the coppery solutions are treated, to the other part, the communication being effected in the manner stated under *l, l*.
m, m, m, m. Floors of wood for convenience in working.
n, n, n, n. Boilers for concentrating the acids serving also as receptacles of the coppery solutions, until they are sent to that part of the refinery appropriated to the manufacture of sulphate of copper.
o. Chimney.

Fig. 78. Vertical section of the refinery on the line A B, fig. 79.



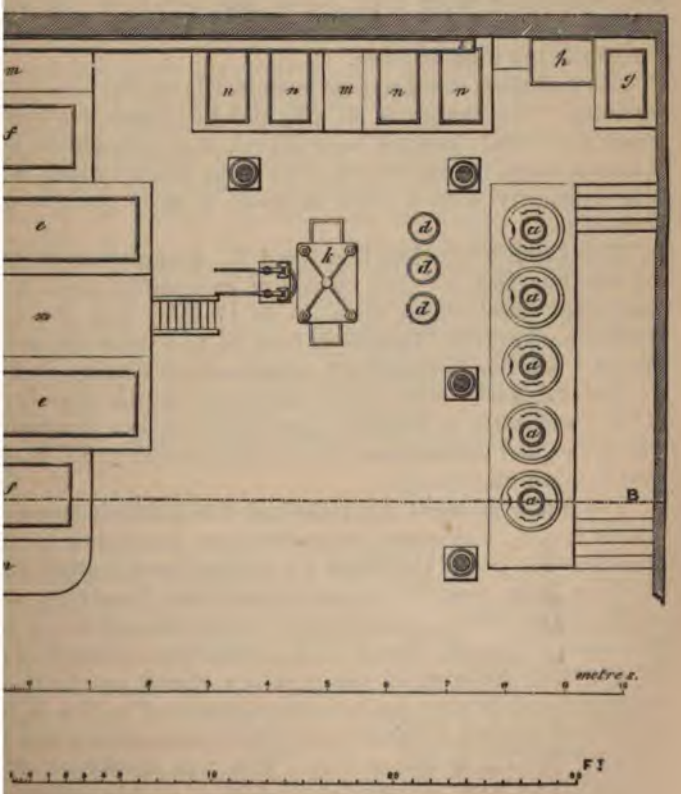


Fig. 79. Plan of the refinery.

the woodcuts figs. 78 and 79 have been prepared on a reduced scale; and although it would now be regarded as somewhat antiquated, yet it may serve the purpose of useful illustration.

The refinery was divided into two parts, which were separated from each other by a courtyard; one being appropriated to the operations connected with parting, and the other to the manufacture of sulphate of copper.

The refinery was originally intended for the extraction of gold from the silver obtained by cupelling the lead produced in smelting auriferous galena, but served also for the refining of foreign coin, gold and silver jewelry, and goldsmiths' ingots resulting from the melting of old jewelry. The products of the refinery were silver and gold, each 997 fine, and sulphate of copper. In the ordinary course of work the substances which contained more than 6–1000ths of gold were treated in the following manner.

MODE OF CONDUCTING THE PROCESS.

The substances above mentioned were divided into two classes:—1st, those containing from 6 to 750 of gold per 1000; and 2nd, those containing more than 750 of gold per 1000, the latter being reserved for the end of the operations. In describing the process I shall use the present tense.

The first class of substances is melted in air-furnaces in plumbago crucibles. The charge is 30 kil., and the fusion requires 3 hours. When the metal becomes very liquid, it is granulated by pouring it into a large copper vessel filled with water, which a workman stirs constantly with a piece of wood, so as to produce a gyratory movement.

The water which has been used for granulation is conveyed to the washing tank *h*. The charge of granulated metal for a single dissolving vessel varies from 15 to 17 kil.; and the quantity of sulphuric acid (of 50° Baumé) is from 2½ to 3 times the weight of the charge. Solution is completed, with constant stirring, in 2 hours.

The sulphuric acid which condenses in the chamber *c* marks 27° B.; and when a sufficient quantity of it has accumulated, it is withdrawn and concentrated in a leaden boiler to 50° B., so as to be used in fresh dissolvings.

The liquor is laded from the cast-iron dissolving vessels into the vessels *d*, *d*, *d*; and when its temperature has fallen to 30° C., it is transferred to one of the tanks *e*, *e*, charged with boiling water. Each of these tanks receives the contents of two dissolving vessels, and ought not to contain more than 35 kil. of fine silver: it is solely on this account that the charge in the dissolving vessels does not exceed 17 kil. The contents of the tank are stirred constantly until the solution becomes very uniform throughout. The fire is then withdrawn and stirring continued for a short time, after which the liquor, marking 17° B., is left at rest. The gold slowly subsides to the bottom of the tank, carrying along with it a little sulphate of silver, and also sulphate of lead when cupelled silver is the subject of

reatment. After the lapse of an hour, the liquid contents of the ank are drawn off by a leaden siphon into one of the precipitation anks *f*, *f*, but not below the depth of 0^{m}·25 above the bottom. In hese tanks are arranged plates of copper. The silver is completely recipitated in 7 hours. The solution of sulphate of copper, which narks 20° B., is drawn off with a siphon and returned to the tank *e*, o serve a second time for dissolving sulphate of silver and for a econd precipitation. When the liquor has been used twice, it marks 24° B., and is sent to the other part of the refinery appropriated to he manufacture of sulphate of copper.

After the coppery solution has been drawn off, the silver is ransferred, by means of large ladles, to the tank *h*, and washed with ot water from the boiler *g*, the whole being constantly stirred with large wooden spatula. The bottom is made slightly inclined, in rder that the water may remove the impurities and the sulphate of opper, and leave the silver pure on the upper part of the bottom. The removal and washing of the silver from a single precipitation requires an hour, the amount of fine silver varying, as previously tated, from 30 to 35 kil. This precipitated silver is designated "chaux d'argent." The wash-water, containing already some sulphate of copper, is transferred to the tank *e*. The washed silver is strongly compressed in the hydraulic press *k*, and comes out in the form of very compact brick-like cakes (*briquettes*), not retaining more than from 8% to 10% of water. The cakes are dried over the melting furnaces, fused in plumbago crucibles, and cast into ingots weighing 20 kil. each, or granulated, according to requirements.

After the lapse of a certain number of days' work, depending on the richness of the matters treated, when the weight of gold in the tank *e* amounts to 4 or 5 kil., it is taken out, dried, mixed with substances containing more than 750 parts of gold per 1000 reserved for this purpose, and melted with 3 times as much silver by weight as there is of gold in the mixture. The molten metal is granulated, boiled with sulphuric acid of 50° B., the gold left to settle down, and the silver precipitated apart. The deposit thus obtained is fine gold, which is washed, dried, and cast into ingots. Cupelled auriferous silver is used for inquartation, but not the precipitated silver free from gold.

MANUFACTURE OF SULPHATE OF COPPER.

The coppery solution, of 24° B., is evaporated to 40°, and then run off into crystallizing tanks (in the following account, in order to avoid confusion, the letter B., indicating Baumé's areometer, will be omitted). After cooling, the products are crude sulphate (A), and mother-liquor (B) of 38°. (A) is dissolved in fresh water; and the solution, which marks 24°, is concentrated to 45°, and run off into crystallizing tanks. After cooling, the products are (A′) merchantable sulphate, and mother-liquor (B′) of 33°. The mother-liquor (B) is concentrated to 45°, when it yields impure sulphate (A^{2}) in the form of a reddish deposit, and sulphuric acid (B^{2}) of 45°: this acid is con-

centrated to 50°, and goes back to the refinery. (A^2) is dissolved in water, and the solution, which marks 24°, is concentrated to 40°, and crystallized: the products are crude sulphate (A) and mother-liquor (B) of 38°. The mother-liquor of 33° (B′) is concentrated to 40°, and crystallized: the products are crude sulphate (A) and mother-liquor (B) of 38°.

The merchantable sulphate of copper, from all these operations, is detached and drained on plates of lead pierced with holes.

It should be stated that at first sulphate of copper was only obtained as a residual product at the refinery of Septêmes, but that afterwards it was attempted to combine the usual method of parting with the manufacture of that salt on a large scale. I have not, however, considered it necessary to present a translation of that part of the original description concerning this exceptional course of proceeding. I have also omitted all the details respecting the costs of parting and of the manufacture of sulphate of copper, which are given at great length in the original, because the results are not applicable at the present day.

Apparatus proposed by Messrs. Johnson, Matthey, and Company, for Parting by Sulphuric Acid.

This apparatus is a vessel of platinum, such as is represented in vertical section in fig. 80. It is entirely open at the top, cylindrical in the upper part and rounded off at the bottom, and contains a central hollow platinum cone, the base of which is fixed to the circumference of a large circular opening in the bottom of the vessel. The cone is perforated with numerous small round holes in parallel rows at right angles to its axis; and round the base of the cone there is a row of similar holes in the bottom of the vessel. To the top of the vessel is attached a hook on each side, by which it may be lifted by means of a semicircular rod of iron, hooked at each end. The weight of such a vessel, including the cone, as is shown in fig. 80, *a a*, is about 250 troy ounces.

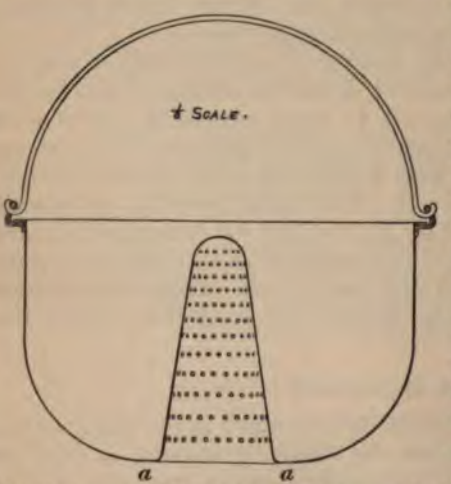


Fig. 80. Apparatus of Messrs. Johnson, Matthey, and Co., for parting by sulphuric acid.

The granulated alloy to be parted is placed in the vessel, which is then lowered into an ordinary cast-iron parting pot containing boiling sulphuric acid, which gains access to the alloy through the

holes in the cone and in the bottom of the vessel, and rapidly dissolves the silver. When this first dissolving is completed, the vessel is raised, and a little cold sulphuric acid is poured over the residue of gold in order to condense the white fumes from the boiling acid, after which it is immediately placed over a leaden pan and washed. The washing is effected in 10 or 12 minutes without disturbing the gold. The vessel containing the washed gold is plunged into a second pot of boiling sulphuric acid, and left there until the operation of dissolving is finished. The vessel represented in fig. 80 is capable of receiving 3000 ozs. of parting alloy, containing 1000 ozs. of gold.

The advantages claimed for this apparatus are stated to be the following:—

1. Great saving of time, only half as much time being required as in the ordinary method.

2. The gold residue being untouched from the beginning to the end of the dissolvings and washings, retains its spongy state, which is alleged to be a great advantage in the subsequent treatment.

3. The use of this apparatus does not necessitate any alteration in an existing plant.

Parting with the use of this apparatus has, I am assured, been most successfully conducted for a considerable period in Messrs. Johnson, Matthey, and Company's refinery.

The apparatus is the invention of my friend and former student, Mr. Edward Matthey, a member of the above-mentioned firm.

Gutzkow's Method of Parting by Sulphuric Acid.

I am indebted to my friend Mr. Frederick Gutzkow for the following interesting and elaborate description of the process of parting by sulphuric acid, which he introduced, and which was adopted in 1867 at the San Francisco Assaying and Refining Works; and I may mention that in 1863 I had the pleasure of receiving Mr. Gutzkow into my laboratory, where he worked for a short time, until he left for California. In a letter to me, dated San Francisco, January 20, 1876, Mr. Gutzkow states that all the operations and apparatus, about to be described, are his own invention; and that he has been careful to omit everything of which any other persons might claim to be the inventors. But he includes in his description an account of Reynolds's process of bar-refining, which has not, to his knowledge, been previously published, and the publication of which in this volume has been authorized by Mr. Reynolds himself.

Gutzkow's method of parting has been patented both in the United States and in Europe.[1]

The refining of gold and silver is extensively carried on by the United States Government at their mints in Philadelphia, San

[1] The English patent is dated June 17th, 1869, No. 1868, and is stated to be a communication from abroad to William Robert Lake, by Frederick Gutzkow, of San Francisco, California, United States of America. The title is "Obtaining Fine Silver."

Francisco, Carson, and at the United States Assay Office in New York. The mints at Philadelphia and San Francisco use the nitric acid process, but the small mint of Carson, Nevada, and the New York Assay Office use the sulphuric acid process.

The leading private establishment in the United States is that of the "Pacific Bullion Exchange," formerly the San Francisco Assaying and Refining Works, at San Francisco. Their refinery was built about twenty years ago (*i.e.* before 1876) by a Hungarian firm, and passed into the hands of the energetic firm of Messrs. Kellogg, Newston, and Co., who placed the refining business on a sound and prosperous basis. In 1866 it was purchased by the San Francisco Assaying and Refining Co., who lowered their charges below London rates. When it is considered that acid, fuel, labour, in fact everything, costs here twice or three times as much as in London, it may be concluded that either the process as practised in San Francisco is superior to that used by European refiners, or that the profits of the latter are very high indeed. It would not be complimentary to the skill of English and French refiners to attribute the great secrecy in which they hold their operations to any other but the last-named reason. The Assaying and Refining Co. becoming involved in the failure of the Bank of California, in 1875, the refinery became the property of Messrs. Flood and O'Brien.

In 1867 the old process of precipitating the silver by copper was superseded by another, which proved more economical, and did away with the unprofitable and troublesome manufacture of blue-stone (cupric sulphate). This new process has been in exclusive operation ever since, and more than a thousand tons of fine silver have been parted by it: and it may here be premised that it consists in separating the sulphate of silver by crystallization, and reducing it afterwards to the metallic state by green-vitriol (ferrous sulphate).

The crude gold (in value about 20 millions of dollars yearly) is received in San Francisco from California and the adjacent states and territories in bars, cast and stamped by assayers in the interior, and is on the average 900 fine, with 1 to 2 per cent. of base metal. The "silver doré" comes mostly from the Comstock mines, which produce very fair bullion, 990 fine in gold and silver, with generally not less than 2, but frequently as much as 10 or more, per cent. of gold. Some other districts, Reese River for instance, send bars with only traces of gold, 800 fine in silver, the balance being copper. The works which treat the tailings from the Comstock mills turn out bullion with from 1 to 2 per cent. of gold and 15 or more of copper. Mexico sends its dollars, celebrated the world over for liberality in weight and assay, with just a trifle of gold, not worth mentioning, per dollar, but agreeably surprising when parted by the ton. Japan sends occasionally its quaint square coins, containing 250 of gold per 1000 and no copper, for refining; but there seems to be an end to the stock of coin in that country, as other people engaged in the Japanese trade have found out.

The bullion is assorted in the following three classes:—1. Gold

bars, which are melted and granulated with Comstock and low grade silver to produce a proportion of nearly 2 parts of gold to 3 of silver, with a small percentage of copper. This alloy is probably the richest in gold that is anywhere subjected to parting, and was originally adopted when refinable silver was only sparingly obtained in the San Francisco market. When properly treated, it yields gold of not less than 990 fine (which is the standard required by the United States Mint), in large and hard grains, exceedingly well adapted for sweetening (*i.e.* purifying by washing after parting), pressing, and melting. An experienced refiner will correctly predict the fineness which the gold will show after melting, within one-thousandth, from its appearance when still in the refining pot. 2. Comstock silver bars, which are parted *per se*, just as they come from the mine, chips being cut for assay. Formerly they were granulated with an addition of copper (or of low grade bars when on hand), and yielded gold of 960 to 980 fineness, which had to be melted with silver and copper and granulated, like crude gold, as described above. Besides, the gold was frequently "mushy," that is, soft and powdery, sweetening slowly, and settling with difficulty in water or acid. In 1865 Mr. John Reynolds, an intelligent workman, suggested the refining in bars. Of course there was no doubt that even the heaviest bars would finally dissolve in hot sulphuric acid; but nobody then believed that a bar weighing nearly 100 pounds, 12″ long, 6″ broad, and 5″ high, would dissolve in less time than when granulated. The result was, however, surprising. The charges of the refining pots could be raised from 140 lbs. to 200 lbs. by operating upon bars instead of granulated metal; the dissolving was finished in 4 hours, as previously; the gold turned out after the first and only boiling of a wonderfully uniform fineness of 996; and last, but not least, the gold was hard and not "mushy," settling and sweetening rapidly. 3. Bars containing much copper, which are melted with higher grade bars until a proportion not exceeding 12 per cent. in copper is obtained. They are not granulated, but cast into bars, about 1″ thick, and yield, by Reynolds's method, gold about 992 fine. The charge of the pot has to be somewhat smaller, in order to finish the parting in the same time as a charge of Comstock bars would require. It may be remarked here that the presence of a small percentage of lead rather facilitates than retards the dissolving of such coppery bars. Sulphate of lead is much more soluble in highly concentrated boiling acid when saturated with silver, than is generally assumed. There is no trouble at all in refining silver bars with as much as 5 per cent. of lead, excepting that the resulting gold is very brittle. The usual method in San Francisco of toughening fine gold bars is by sal-ammoniac and (in stubborn cases) by a weak blast on the surface of the molten metal, which is most effectual in removing lead from gold.

All the three methods above briefly referred to will surprise some European refiners. The treatment of an alloy containing so large a

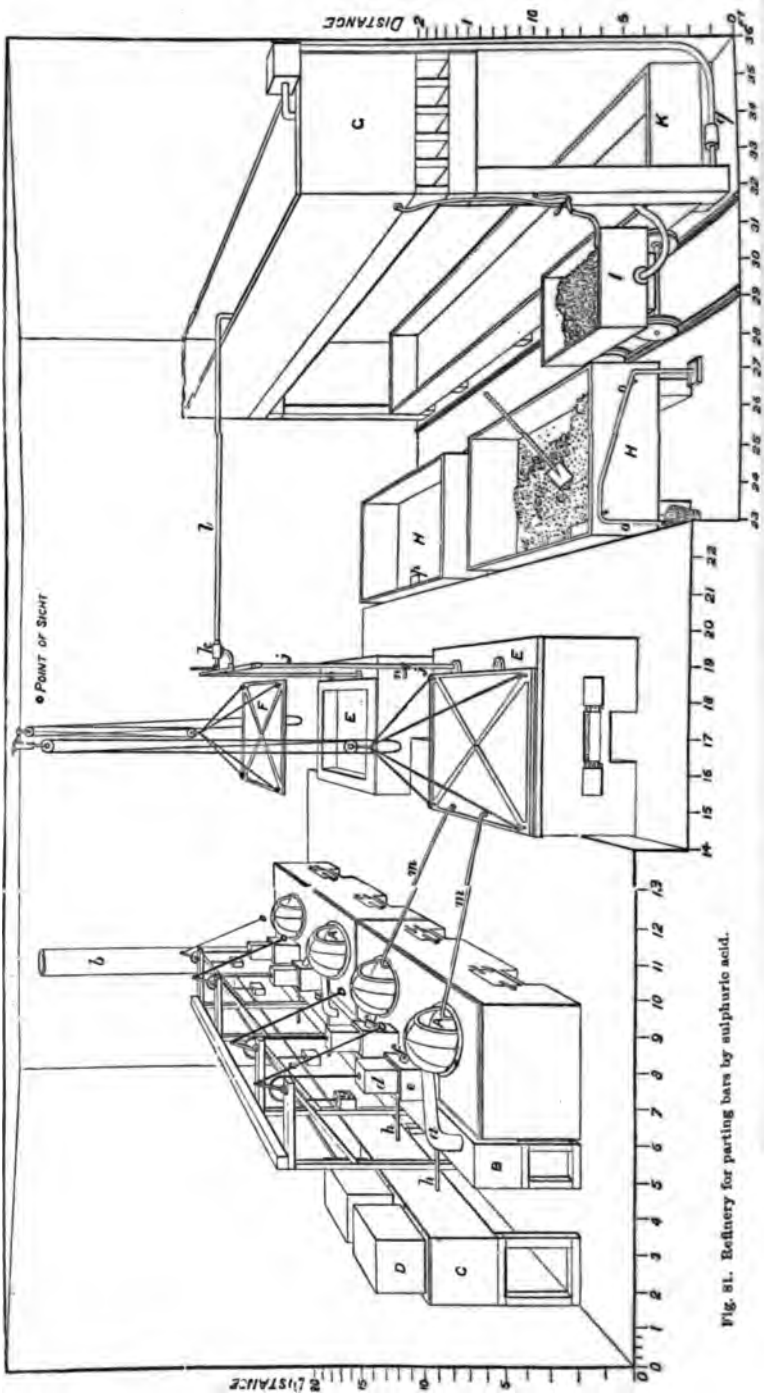


Fig. 81. Refinery for parting bars by sulphuric acid.

proportion of gold, and the obtaining of fine gold from heavy silver-bricks in one boiling of 4 hours, are far from usual in European practice. The secret lies to a great extent in the character of the Californian refining pots (*i.e.* the cast-iron dissolving pots), which differ essentially from those used in other places. They are much smaller, less than 2′ in diameter, and still less in height; they are also much thinner, being when new only $\frac{3}{4}''$ thick, and, in the course of two years, wearing off to a uniform thickness of $\frac{1}{4}''$. The bottom is not rounded, but flat, thus presenting a larger surface to the fire, and exposing the gold in an even and low layer to the action of the heat. Such pots are much more economical with respect to fuel than the large, thick, and heavy pots in use in Europe. The acid is brought to the boiling-point in a very short time, and kept boiling from beginning to end as briskly as the height of the pot will admit of. Uniformity in working is insured by the judicious addition of acid in small quantities and at regular intervals.[2] Oak-wood is used as fuel, and consumed at the rate of 1 cord (8 × 4 × 4 feet) per 2000 lbs. of bullion.

In the following description the letters in the accompanying perspective woodcut, fig. 81, are referred to.

The refining pots A are placed in a row of four in a furnace, encased in cast-iron plates. Each pot has its separate fire-place, and is covered by a cast-iron dome, from which the lead pipe *a* leads to a closed tank B, and thence through the larger pipe *b* to the condensers, in which a powerful draught has to be maintained. The sulphuric acid is contained in the tank C, and supplied to the refining pots A in the following manner:—A $\frac{3}{4}''$ pipe *h* forms a connection between the acid tank C and the lead-lined bucket *e*. In both the acid stands at the same level. The carboys D rest, bottom up, on the tank C. The necks dip about $\frac{1}{2}''$ into the acid. Thus only when the level of the acid sinks can air enter the interior of the carboy and allow fresh acid to escape. As soon as the rise of the level closes the opening of the carboy, the escape of acid is stopped. There is always a considerable number of carboys resting bottom up on the tank C; but in the woodcut only two are represented. Now, by pulling the iron rod *c*, the plunger *d*, a solid wooden block covered

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[2] Regarding refining in bars, it is obvious that silver bars present for a comparatively long time the same small surface to the acid, and are more equably heated than granulated silver, which requires a constant watching and regulation of temperature, the workmen having good reason to fear the responsibility, extra work, and occasionally actual bodily danger from a boiling over. In ordinary cooking, only the watching of milk-boiling may be compared with the dissolving of granulated silver, which contains no copper. Besides, in bar refining, the particles of gold, as they are laid bare, are always exposed to the full action of the boiling acid, whereby they aggregate into larger grains on the very surface of the bar, and are never covered over with undissolved silver. Mr. Reynolds's method is decidedly simple, and (of course) known to everybody, just as was Columbus's method of placing an egg upright, but I can assert that there is in it much good sense, merit, and pecuniary advantage.—F. G.

with sheet-lead, sinks down into the bucket *e*, which allows a play of 2″ all around the plunger. Some iron rods, not shown in the figure, insure accurate vertical movement. The weight of *d* must be a little greater than that of the acid displaced, which is forced up and escapes through the overflow pipe *f*, measuring 3″ in diameter, into the refining pot. A small portion is, of course, also forced back through *h* into the tank C. On letting go the rod *c*, the counter-weight *g*, a solid lead-brick, raises the plunger *d* back to its old position, when a fresh supply of acid is brought through *h* from C, until the original level is restored. Each discharge of the bucket brings 20 lbs. of acid into the pot A, and requires only a few seconds, whilst the refilling is effected in half a minute.

At 7 A.M. 200 lbs. of silver bars or granulated gold alloy are placed in each pot A, and dissolved in 4 hours after the addition of 300 lbs. of acid, which is added at the rate of one bucketful every 15 minutes. The gold remains as a hard and heavy gravel, the further treatment of which will be described hereafter. The silver-solution is then siphoned off into the cast-iron pan E, which is provided with a fire-place and encased in iron plates like the refining furnaces. An underground flue leads to the stack of the latter, neither of which is shown in the woodcut. An iron plate F covers E, and can be raised by the tackle *i*. The pan E has a capacity of 50 cubic feet, and is filled to within 3″ of the top with the mother-liquor from a previous crystallization, which consists principally of sulphuric acid, of 58° Baumé, heated to about 250° F. The iron pipe *j* leads from the tank E to the steam-jet suction apparatus K, which with 60 lbs. pressure of steam can produce a vacuum of 18″ mercury, in about 1 minute, within E. From *k* the mixture of steam and air escapes through *l* into the tank G, where it discharges through a perforated lead pipe into the liquid with which G is filled. A rubber band, 4″ broad, is placed between the rim of the pan E and the cover F, which, during the pumping operation, is compressed by the joint weight of the cover and that of the atmosphere and prevents any leakage of air into E.

The bent gas-pipes *m* serve as siphons (or suction-pipes) from the refining pots to the pan, and enter F air-tight by means of rubber packing. By turning steam on in *k* and opening the stopcock *s*, the air is exhausted in E, the siphons are charged, and the liquid contents of the two refining pots rapidly transferred to E. It may be here at once remarked that the pumping up of the mother-liquor from H to E is effected in precisely the same manner, the iron pipe *o* being placed in position to form the connection between the two tanks. The manner of pumping just described has decided advantages over the well-known "montejus" (a machine for raising liquids by the direct action of high-pressure steam), as there are no screws and bolts to prevent a rapid and frequent inspection of the interior of the apparatus; and, besides, a third vessel in addition to E and H is avoided, which is always desirable in a gold-refinery. The apparatus *k* is the simplest possible, and all the steam is utilized in the tank G.

As soon as the liquid contents are transferred from the refining pots the pan E, the cover F is raised, the rubber-band removed (which prolonged contact with the pan E, although the latter is only oderately warm, would lose its elasticity), and a few bucketfuls of stilled water are added, an operation which can be effected without nger of splashing. Sufficient water must be added to reduce the ecific gravity of the fluid, which was increased, by the addition of e highly-concentrated acid from the refining pots, again to 58° B. f course, independently of the sulphates dissolved); otherwise, cooling, the silver would be separated, partly or wholly, as a sulphate, which on contact with water would form a powder taining much free acid, and would in that state be entirely unfit r further treatment. The object is to separate the silver as a mono-lphate as hard as possible, from as acid a solution as possible, r which 58° Baumé is about the limit. Above that strength the rmation of bisulphate begins, never below. The addition of water the contents of E serves also essentially to purify the solution. ny sulphate of lead still dissolved is, practically, wholly precipitated, id the cloud of sulphate of silver produced by the dilution with ater clears the solution most rapidly of all suspended matter. The on, which was present in the strong silver-solution as an insoluble utral sulphate of peroxide and caused its yellow and muddy pearance, absorbs water in the weaker acid and settles as a eenish basic sulphate. Once every month the sediment covering e pan E to about the height of 2″ is removed and dissolved in ater. It consists of sulphates of iron, lead, and silver, some gold, id a graphitic substance derived from the cast-iron pots and tools. he residue, after treatment with water, is mixed with some granu-ted zinc to reduce the sulphate of lead, and, after having been ashed and dried, is melted in a small reverberatory furnace with e addition of carbonate of soda, no other flux being able to remove e graphite so rapidly.

Each refining pot described above loses about 150 lbs. per annum weight, or $\frac{1}{4}$ lb. per 100 lbs. of silver refined. The higher or wer concentration of the sulphuric acid causes some, but not very portant, variation in the action on the pot. From a large pot ss iron will be dissolved in proportion than from a smaller one. the laboratory, the refining process cannot be properly imitated at l by dissolving, say, a few ounces of silver, owing to the copious diment of sulphate of iron formed.

The purified and clarified solution in E is ready for further eatment a few minutes after the addition of water. It is siphoned ff into the cast-iron open pan H, $5' \times 7' \times 1\frac{1}{2}'$, for crystallization. n San Francisco work is suspended during the night, and that peration generally finishes the day's work. In the morning the lution in H is found to have cooled down to about 80° F., which is fficient; by artificial cooling, however, or by employing several rystallizing pans, for each solution pan a more rapid working can, of ourse, easily be effected. The mother-liquor is pumped up into E in

the manner described; a deeper cavity *p* left in the cast-iron pan H, serving as a well for the pipe *o*, and allowing the last drops of acid to drain off. The sulphate of silver is found to cover the surface of the pan H in a crust from 1″ to 2″ thick in hard yellow crystals, which retain very little free acid, and somewhat resemble in shape the beard of a quill; and mixed with them is a reddish powder of sulphate of copper. [An analysis of this powder is to be desired.—J. P.] Owing to the addition of free acid from the refining pots and of water, the mother-liquor has much increased in bulk, and the surplus is divided in a suitable manner among the refining pots. Thus, all the free acid left after dissolving the silver or that recovered in the condensers is completely and economically used over again. Once a year, at the annual settlement, the mother-liquor is diluted to 25° B., desilverized by copper, and used in the manufacture of bluestone (cupric sulphate) from the precipitated copper accumulated during the year. The new account, then, opens with fresh acid of 58° B.

The crystals of sulphate of silver are taken from the pan H by means of a common iron shovel, and thrown into the filter-box I, which is provided with a false bottom made of wood, or better of plates of porcelain, perforated with holes $\frac{1}{8}$″ in diameter. A layer of precipitated silver, spread over the false bottom, serves as a filter. Now, a stream of a hot solution of green vitriol of 25° B. is admitted from the tank G and allowed to percolate the crystals, converting them into a very heavy and dense mass of metallic silver, which retains the shape of the crystals. The sulphate of protoxide of iron is converted into sulphate of peroxide ($2(FeO,SO^3)+AgO,SO^3 = Fe^2O^3,3SO^3+Ag$ [idem, except the substitution of Ag^2 for Ag]), the colour changing from green to an intense coffee-brown. The oxidized iron solution discharges into the lead-lined tank K, which ought to be capacious enough to hold all the liquid required for reduction (*i.e.* about 100 cubic feet for 500 lbs. of silver). The first portion percolating the crystals, although highly charged with sulphate of peroxide of iron, has a bluish colour, from the sulphate of copper first passing into solution. It runs into another tank placed in one line with K, but not shown in the figure, and is there precipitated by copper. After the precipitate has settled down, the solution, to which some salt has been added for the sake of safety, is taken to another building, and there deprived of its copper by means of iron. To the brown iron solution retained in K some sheet-iron is introduced after it has cooled, heavy and large pieces being preferable, when the peroxide is again reduced to protoxide ($Fe^2O^3,3SO^3+Fe = 3(FeO,SO^3)$ [idem]). Previous to a new operation, it is pumped up into G by means of the steam-jet-pump *q*. It will be perceived from the foregoing description that the solution of green vitriol suffers only a temporary change and may be used over and over again for many years, in fact for ever. The surplus which each operation furnishes is removed by the bluish liquid mentioned above, which carries away also the largest amount of the free acid that may have adhered to the crystals in I. The more neutral these crystals and the solution of

green vitriol are, the more rapid is the reduction. The reduction of 700 or more pounds of silver, which the filter box I, that receives the total yield of the four refining pots, contains at a time, is finished in about 3 hours. There is no labour involved excepting an occasional turn-over, and one man may attend to a considerable number of filters. In the brown as well as the bluish solution of peroxide of iron is deposited on cooling a large portion of metallic silver from the sulphate of silver dissolved, there being always enough sulphate of protoxide of iron left to complete the reaction, which takes place more rapidly in the filter itself. Of the above 700 lbs. of silver 90 per cent. are retained in the filter, $7\frac{1}{2}$ per cent. separate on cooling, and $2\frac{1}{2}$ per cent. are regained by iron from the brown, and by copper from the bluish, liquid. Those 10 per cent. are removed from their respective tanks on the following day, and used to form the filter of metallic silver in I mentioned above. The metallic copper which the metallic iron will precipitate in K (the largest portion having been removed as sulphate in the bluish liquid) is rapidly dissolved in contact with the sulphate of silver. The reduction of the sulphate is considered finished, when the iron-solution leaves the filter-box I with a pure green colour, and contains no silver. Sometimes it is found more advantageous not to reduce the last traces of sulphate of silver, but to place the silver in another filter-box of similar construction, with a layer of old ship's copper between every 2″ of silver, and to sweeten with hot distilled water. Not a trace of dissolved silver will escape from the filter-box with the water. When, however, the silver in I is perfectly reduced, the copper plates may be omitted, and common hot water employed. The sweetening is discontinued when yellow prussiate of potash fails to cause a blue precipitate.

The filter-box is then run to a hydraulic press, where, under a pressure of about 8000 lbs. to the square inch, the silver is converted into round cakes 3″ thick and 10″ in diameter, which are dried in iron pans in a kind of reverberatory furnace heated with wood. The silver reduced by green vitriol is much heavier and more compact, when pressed, than that precipitated by copper. One cake of the first weighs 30 lbs., whilst one of the latter weighs only 22 lbs., both being of the same dimensions, and having been subjected to equal pressure. The dried cakes are melted down in plumbago crucibles, holding 150 lbs. of silver, with the addition of some borax, toughened by the addition of a very little nitre, and cast into bars.

In the preceding description the gold was left in the refining pots after the silver-solution was siphoned off. When obtained from the granulated alloy, it is boiled a second time in a smaller quantity of acid, which, however, takes up very little silver, and which is left in the refining pot to serve instead of fresh acid in another operation. It has already been remarked that the gold from the refining of bars is 996 fine at the first boiling, and needs no second boiling at all. The gold obtained in either way is taken from the pots with iron ladles as hot as possible, and placed in a cast-iron pot running on

wheels and containing some hot concentrated acid, whence it is conveyed into a filter-box filled with hot water. A better method, however, is the following:—A lead-lined filter-box is half filled with acid obtained from the condensers, which is generally of the strength of about 45° B., and contains a little silver, that acid having previously been heated by steam, and run into the refining pot. The hot gold is baled through a funnel reaching through the cover; the acid, the strength of which has greatly increased by the addition of the acid carried over with the gold, is run into one of the pans E; the filter-box is removed to another part of the building, specially destined for the sweetening operations; and the gold is made sweet with hot distilled water in the same apparatus. In this manner some apparatus is rendered superfluous, one moving of the gold saved, the direct mixing of the hot gold with water avoided, and the silver in the condensed acid and the latter itself are properly utilized. As a false bottom for this filter-box plates of porcelain with $\frac{1}{2}$" holes may be used, but a row of $\frac{1}{2}$-round iron rods covered with lead pipe placed over some proper support answers very well.

When sweet, the gold is pressed into cakes and dried like the silver, melted in plumbago crucibles, holding 300 lbs. of gold, with the addition of a little borax, toughened with a few lumps of sal-ammoniac, and cast into bars.

SUMMARY OF THE PROCESS ABOVE DESCRIBED.

I. The substances treated are of three kinds, namely, (*a*) gold bars, (*b*) Comstock silver bars, and (*c*) coppery bars.

II. The gold bars (*a*) are alloyed with a due proportion of silver and granulated.

III. The silver and coppery bars (*b* and *c*) are not granulated, but cast into bars and parted in that form.

IV. The dissolving is effected in cast-iron vessels, flat and comparatively thin at the bottom.

V. The acid solution of sulphate of silver is diluted with water, when nearly the whole of the sulphate is precipitated in crystals.

VI. The crystals of sulphate of silver are treated with a strong solution of ferrous sulphate, when the silver is separated in the metallic state, with the formation of ferric sulphate.

VII. The reduced silver is washed, strongly compressed, dried, melted, and cast into bars.

VIII. The solution of ferric sulphate, obtained in VI., is heated with metallic iron, when it is reduced to ferrous sulphate, which is used for reducing fresh sulphate of silver.

IX. Washing or "sweetening" the gold in a special apparatus, drying, melting, and toughening by sal-ammoniac (chloride of ammonium).

Projection of minute Particles from a molten Alloy of Gold and Copper during Cooling.

I am indebted to my friend Mr. C. Tookey for the following observations, which he made while engaged as Assayer at the Japanese Mint.

In the Imperial Mint at Osaka, Japan, bars of gold from San Francisco were frequently converted into standard metal for coinage by melting them with the requisite proportion of Japanese copper, to produce an alloy containing $\frac{900}{1000}$ths of gold. In melting one particular consignment there was an unusual loss, as shown by the difference between the weight of gold and copper melted and that of the bars after pouring. No good reason could be assigned for this in the Melting Department, but on investigation Mr. Tookey found that the clay-graphite muffles and stirrers used in the operation were coated with what appeared at first sight to be minute grains of dark red sand, but which on examination proved to be globular particles of the gold-copper alloy. By simply heating them in nitric acid the proper colour of the alloy was at once developed, owing to the removal of the superficial film of oxide of copper. It appeared as though the particles had been projected from the surface of the melted metal by the escape of a gas, *i.e.* by a kind of effervescence, similar to that caused by the liberation of carbonic acid from champagne or soda-water. Mr. Tookey had often watched a similar phenomenon when the pots containing the silver-copper alloy were removed from the furnaces previous to pouring. While one of these pots, holding 2500 ounces and upwards, was cooling on the floor of the melting-room to the proper temperature, a strong effervescence took place at the surface of the metal, projecting it in most minute particles, which were carried by the current of air away from the pot, and accumulated on the floor in sufficient quantity to be swept up. During the effervescence there was a powerful smell of sulphurous acid, which had no doubt been temporarily absorbed or occluded by the metal while the pot containing it had been exposed at a high temperature to the products of the combustion of coke containing much sulphur.

Process of parting highly cupriferous Alloys by Sulphuric Acid, as formerly practised.[3]

In this process, which was formerly much used, highly cupriferous alloys of silver and gold, or such as varied in fineness from 360 to 500 (*i.e.* contained from 640 to 500 parts of copper per 1000), were subjected to the following preliminary treatment, whereby sufficient copper was removed to render what remained suitable, in composition, for parting in the ordinary manner. The granulated alloy is made

[3] This process has been designated "pagamentation," which is derived from the Italian word *pagamento*, which is technically applied to silver of low standard.

red-hot in a flat-bottomed reverberatory furnace and rabbled, whereby it is further divided; but if the alloy is in the form of coin, granulation is omitted. In this operation the copper in the outer part becomes oxidized. The alloy is then boiled in sulphuric acid, diluted to 15° Baumé, in order to dissolve the oxide of copper produced. The residual alloy, now become relatively richer in silver, is taken out of the acid solution and washed with water on a sieve, when a portion in the state of slime, richer in silver than the remainder, passes through. The coarse particles left on the sieve are treated precisely like the original alloy in the first instance, that is, are heated to redness, boiled with dilute sulphuric acid, etc.; and this series of operations is repeated until the whole of the undissolved residue is converted into a slime rich in silver, *i.e.* from about 850 to 900 fine. This slime is washed, dried, heated to redness, and then parted by boiling in the usual way with strong sulphuric acid.

Owing to the large expense of time required in this process—the heating to redness and subsequent treatment with dilute sulphuric acid having often to be repeated 6 or even 8 times—and to the accompanying great and unavoidable loss in metal, it has been nearly everywhere abandoned. At present highly cupriferous or low grade silver is reduced to particles of suitable size, and directly dissolved in concentrated sulphuric acid. As bars of such an alloy are brittle at a red-heat, their comminution is best effected by pounding them, while red-hot, in an iron mortar, separating the finer particles by sifting, and repeating this treatment upon what remains on the sieve until the whole of the metal is sufficiently pulverized. When the powder thus obtained is properly stirred up in the boiling sulphuric acid in the parting pots, it may be completely converted into sulphates.[4]

Partial separation of copper from highly cupriferous alloys of silver and gold by heating with nitre.—This process, designated "poussée" by the French, was extensively practised in former times in French parting works. The ingots were broken, while red-hot, into pieces, and melted in crucibles with the addition of $\frac{1}{10}$th of their weight of nitrate of potash. The molten metal was cast into ingots, and immediately afterwards subjected to the same treatment as that just described; and this treatment was repeated until sufficient copper had been removed to render the alloy suitable for boiling with sulphuric acid.

The alkaline slag, formed in the fusion, was found by Berthier to contain cuprous oxide, oxide of silver, and metallic silver. Lebel, who according to Dumas was one of the most skilful French refiners of the day, used this slag to saturate part of the excess of acid contained in the sulphates resulting from the solution of the alloy in the parting vessels, which then consisted of platinum. By this means, the sulphuric acid in excess changes the cuprous oxide into metallic copper and cupric sulphate; the metallic copper thus formed, which is very finely divided, forthwith precipitates silver from part

[4] The foregoing description is from the pen of Dr. Rössler.

f the sulphate of silver; the oxide of silver in the slag is converted ito sulphate, which is also decomposed by the copper; and the etallic silver intermixed with the slag becomes associated with the lver precipitated by the copper.

Berthier proposed to substitute for nitrate of potash twice its eight of crystallized cupric sulphate, in which case the resulting ag "would be composed of cuprous oxide united to oxide of silver, hich would render the slag fusible. This slag, poured into the acid ılphates, would behave like the former (*i.e.* that resulting from the se of nitrate of potash). The copper would play a double part in ie operation: it would act as a reducing agent in the precipitation, ıd as an oxidizing one in the 'poussée.' There would be a veritable ionomy in nitre, as it would be replaced by a product which would ways be recovered, save what is unavoidably lost." [5]

XTRACTION OF COPPER FROM HIGHLY CUPRIFEROUS ALLOYS OF SILVER AND COPPER, WITH THE USE OF SULPHUR AND DILUTE SULPHURIC ACID.

SERBAT'S PROCESS.

M. Serbat, "private assayer to the Director of the Mint at Paris," otained a patent in France in 1824 for a process of separating pper from silver with the use of *dilute* sulphuric acid, and which considered might be applied with advantage to the parting of loys of silver and copper of low standard.[6]

The following is a description of the process:—The alloy is heated a cast-iron muffle to the temperature at which it becomes brittle, ıd is then crushed by striking it with a rabble. The product is fted in a bolting machine, provided with wire gauze, in order to parate the largest fragments; and the powder which has passed rough is heated to brown redness (*rouge brun*) in another cast-iron uffle set in a reverberatory furnace. After having spread the wder in thin layers, 25 per cent. of its weight of sulphur is ojected upon it and the whole is well rabbled. Combination takes ace almost instantaneously, with evolution of heat and light; and hen it is finished, which may be easily known by the cessation of candescence, the resulting sulphides are withdrawn and thrown to wooden vessels filled with water. The cooled sulphides are moved, thoroughly pulverized (*divisés complètement*) by pounding or inding, and sifted under water. The powder thus obtained is ansferred to a large cast-iron muffle set in a reverberatory furnace, ıd placed in that part of the muffle which is least heated; it is

[5] Dumas, Traité de Chimie appliquée x Arts, 1833. 4. pp. 472–3. The eceding statements respecting the oussée" are translated nearly literally m that treatise.

[6] "Mémoire sur un mode de traitement cuivre argentifère, applicable à l'affine des monnaies à bas titre; Par M. Serbat, ancien préparateur de M. Thenard, essayeur particulier du Directeur de la Monnaie de Paris." An extract from this Memoir appeared in the Annales des Mines, 1826. 13. p. 283, and from that extract the description in the text has been derived, as I have not seen the original memoir.

then stirred in order to expose fresh surfaces; and a mixture of 2 kil. of nitric acid to 12 kil. of water per 100 kil. of alloy is projected in successive portions upon the powder. The fumes of nitrous and sulphurous acid which are disengaged in this operation are conveyed into leaden chambers, where they are condensed by the injection of steam frequently repeated, and produce sulphuric acid for use in subsequent stages of the process.

The product in the muffle is gradually heated to redness, and kept for about 4 hours at that temperature, after which it consists of metallic silver, oxide of copper, and, it may be, some undecomposed sulphates and sulphides. After letting the product cool somewhat, it is thrown into a leaden boiler containing weak sulphuric acid, previously heated by injecting steam into it for the purpose of diluting it. The oxide of copper and any undecomposed sulphates are dissolved, whilst the metallic silver, which is not attacked by weak sulphuric acid, collects at the bottom of the vessel, and only requires to be washed, dried, melted, and cast into bars. From the supernatant liquors, which are drawn off by a siphon into leaden boilers, sulphate of copper is produced in the usual manner.

Serbat asserts that this process was adopted with success at the Paris Mint, and at another establishment in the same city, during a period when alloys of silver and copper alloys of low standard were very abundant in commerce, and that on the ground both of economy and rapidity it was greatly to be preferred to any process which had been previously used for parting such alloys.

BERTHIER'S PROCESS.

Berthier, in 1825, suggested the following method of partially separating copper from alloys of silver and copper of low standard.[1] The alloy is to be sulphurized by heating it with the addition of sulphur, and the product treated as in the process of making cupric sulphate from cuprous sulphide without the use of sulphuric acid; that is, roasting it in fine powder in a reverberatory furnace at a duly regulated temperature, washing with water in order to dissolve out the cupric sulphate formed, again roasting the residue, etc. The silver might thus be concentrated in a small quantity of copper; but, adds Berthier, as it would be necessary to repeat these operations many times, the process would be long and attended with the risk of losing much silver. It would, therefore, be certainly preferable to roast the sulphurized product as completely as possible, that is, so as to oxidize the whole of the copper and decompose as little as possible of the cupric sulphate which is formed, a result only to be attained by the most careful regulation of temperature, and then to boil the roasted product with sulphuric acid. If any silver should be dissolved along with the copper, as might perhaps be the case, it should

[1] Sur le traitement métallurgique des alliages de cuivre et d'argent. Par M. P. Berthier. Annales des Mines, 1825. II. p. 120.

be precipitated either by means of some of the unsulphurized alloy, or by copper. By this method a large quantity of sulphuric acid would be economized, and all the difficulties met with in the direct treatment of the alloy by this acid would be avoided.

In 1846 I conducted an experiment on a large scale at the German Silver Works of Messrs. Evans and Askin, on the separation of silver and gold from an alloy consisting chiefly of copper; and as apparatus existed there in which *dilute* sulphuric acid could be heated by the direct injection of steam, but none suitable for the use of *strong* sulphuric acid, it was decided to adopt a process similar to that suggested by Berthier.

The alloy was in the form of rectangular ingots or bars, cast in an open mould. There were 21 of such bars, which varied in weight from 44 lbs. 9 ozs., troy, to 106 lbs. 6 ozs., and the total weight of which amounted to 1627 lbs. 5 ozs., troy. They contained variable proportions of fine silver and gold, the smallest being 53½ dwts. of silver and 3 grs. of gold, and the largest 70½ dwts. of silver and 6 grs. of gold per lb. troy. The total weight of silver in the bars amounted to 5298 ozs., and that of gold to 14 ozs. 18 dwts. The foregoing proportions of silver and gold are those furnished by a firm in London who assayed the bars on account of the seller; but they exceed by about 379 ozs. of silver and 2 ozs. of gold those obtained from assays in my laboratory of portions of the *same* pieces of the bars which had been cut off for the seller's assayer, and the remainder of which was forwarded to the purchaser of the bars.

The bars were sulphurized in the manner previously stated at p. 157, and the product was ground under edge-stones, finely sifted, and roasted *sweet* in a small reverberatory furnace built for the purpose, after which it was heated with dilute sulphuric acid,* by the direct injection of steam. This operation was effected in a large flat-bottomed cylindrical jar of Vauxhall stoneware, set within a vessel of the same form, which was of wrought-iron plate, the space between the two vessels being filled with a mixture of sulphur and sand. Such a mixture is an excellent and durable cement, and is easily applied by heating sufficiently to render it viscous and then pouring it into the space, the jar having been previously warmed to prevent its cracking. The solution of cupric sulphate was siphoned off, evaporated in a leaden vessel, and crystallized. Part of the metallic residue was heated with nitric acid, somewhat diluted, in the same kind of jar as above described, the solution drawn off with a siphon, the silver precipitated in the state of chloride, and the chloride reduced by zinc bars in the manner stated at p. 93. The undissolved residue consisted of gold in admixture with a considerable quantity of the red-brown substance described at p. 26. The remainder, and by far the larger portion, of the metallic residue was parted by sulphuric acid in a cast-iron pot; the acid solution of sulphate of silver was diluted with water and heated by steam, the silver precipitated

* The common "brown oil," as it comes from the leaden chambers, was used.

therefrom in the state of chloride by the addition of hydrochloric acid, and the chloride reduced by zinc bars. The whole of the residue containing the gold was heated with nitro-hydrochloric acid, and the gold thrown down in the metallic state from the solution by the addition of ferrous sulphate.

The result of the preceding experiments was not satisfactory; and there is risk of serious loss, especially in roasting, in the state of fine powder, a substance so rich in silver as that of the sulphurized product in question.

Extraction of Silver and Gold from refined Copper at the Oker Works, in the Harz, by "Vitriolization" (*Vitriolisirung*).

I am indebted to Mr. Frederick Ulrich for a description of this process, which he communicated in 1871, and which is here presented along with additional information extracted from a paper on the subject by Bräuning, manager of the Oker Works, which was published in 1877.[9]

GENERAL DESCRIPTION OF THE PROCESS.

The copper produced in the various operations of smelting at Oker is either rich or poor in silver: the former is pretty strongly impregnated with impurities, which injure its quality, and are difficult to remove, while the latter is free from such impurities. Both of these kinds of copper (*i.e.* in the state of black-copper) had for a long period been kept separate at Oker; and formerly the first kind was subjected to the process of liquation before being refined. But in 1858, that process having at last been found to cost more than the value of the silver obtained, was abandoned, and the process of "vitriolization" has been substituted for it, which consists in converting the copper into saleable blue-vitriol, and thereby separating the precious metals in the form of fine mud or slime. The second kind of copper, or that which is poor in silver (which amounts to 0·07% or nearly 23 ozs. per ton), is, as formerly, directly refined and sold in the form of "rosette copper."[1] The "vitriolization" process having been introduced into other localities, of which Altenau in the Upper Harz is one, scarcely any profit can now be derived from the manufacture of blue-vitriol, so that the establishment at Oker should be exclusively regarded as one for the production of silver.

In the "vitriolization" process the copper is converted into sulphate, and its oxidation is wholly effected by the oxygen of the air, not the slightest decomposition of sulphuric acid being detected during the process. The copper is used in the granulated state, in order that its surface may be very greatly extended, and oxidation promoted in a corresponding degree. The granules are exposed to the combined action of hot dilute sulphuric acid and atmospheric air.

[9] Zeitschrift für Berg-Hütten- und Salinenwesen im Preussischen Staate, 1877. 25. p. 163.

[1] The total yearly produce amounts to 10,000 centners of black copper, about half of which is sold in the state of "rosette copper."

e operation is effected in vats, from the bottom of which the hot
d liquor flows into a long trough, depositing in its course, as it
ls, most of the dissolved cupric sulphate and the fine particles
silver, which it contained in suspension. At the end of the
ugh the acid liquor flows into a tank, from which it is conveyed
o another tank at a higher level; and from the latter, after the
dition of fresh sulphuric acid, it again falls in drops upon the
nulated copper; and so this operation is repeated until the copper
s been wholly converted into sulphate. The deposited cupric
phate, which contains all the silver and gold in the state of mud
slime, is redissolved and crystallized, when marketable blue-vitriol
produced, and a residue obtained from which the precious metals
extracted.

DESCRIPTION OF THE APPARATUS AND PLANT.

Dissolving vats.—They are circular, widening from 2′ 6″ in internal
meter at the bottom to 3′ at the top, and are 5′ deep. The bottom is
t and slopes downwards towards the front, where there is a rectan-
lar opening, 12″ wide and 6″ deep. The vats are made of wood,
d lined internally with sheet-lead, which is prolonged nearly 12″
wards beyond the top or rim, and projects about 6″ beyond the
le at the bottom in front, so as to form a spout. There are 10 of
h vats, set close together in a row, except in the middle, where a
ce of about the width of a vat is left, which serves as a passage,
d divides the vats into two series of 5 in each. The vats are
ced upright, about 2′ from the floor, on a wooden platform covered
th sheet-lead, which slopes downwards parallel to the bottom of
vats, so that in the event of leakage the acid liquor may flow
o the same tank as that from the vats.

Troughs.—Connected with each series of 5 dissolving vats is a
ugh about 340′ long, which very slightly inclines from one end to
e other, and at the furthest or lowest end communicates with a
tangular tank; it is carried forwards and backwards in order to
nomize space; both it and the tank are made of wood, lined with
eet-lead; the trough in the first half of its course, *i.e.* for 170′, is
wide and 9″ deep, but in the other half of its course it is only
wide, its depth remaining the same.

Supply tank for dilute sulphuric acid.—Above and extending along
ch series of dissolving vats is a rectangular tank, made of wood
d lined with sheet-lead, the height of the bottom of this tank above
e rim of the wooden dissolving vats being about 7′. At the bottom
the tank is a leaden pipe, bent backwards and forwards, through
hich steam is passed for heating the acid.

Over each dissolving vat a siphon, made of lead, is suspended by
chain, by which it can be raised or lowered at will; the short leg
the siphon is contained within the supply tank, while the lower
g descends to a few inches below the rim of the upper and
ojecting part of the lead lining of the dissolving vat; the end of
is leg is widened into the shape of an inverted funnel, and is

closed at the mouth with a disc of perforated lead, so that the liquor flowing from it may fall in drops as uniformly as practicable; and a little above this end a stopcock is fixed in the siphon for regulating the supply of acid liquor.

From the preceding description, it will be seen that each series of 5 dissolving vats may be worked separately.

The dissolving vats, troughs, and receiving tanks are arranged on the first floor, while the ground-floor is reserved for the apparatus used in purifying and crystallizing the blue-vitriol in the manner described in the sequel.

MODE OF CONDUCTING THE PROCESS.

The copper subjected to the process of "vitriolization" at Oker in 1871 contained from 0·1% to 0·4% of silver, and on the average 0·166% (54 ozs. 4 dwt. 12·8 grs. per ton). In order to produce a blue-vitriol (cupric sulphate) as pure as possible, the copper is refined in a "Spleissofen," and used in the state of "rosette" copper (*rohgaar*, which corresponds to the "dry" copper of the first stage of refining by the Welsh process). It is granulated in cold water. On the bottom of each dissolving vat is placed a layer, about 6" thick, of copper broken into pieces as large as the fist, which act as a sort of sieve or filter. Upon this layer the granulated copper is piled to the thickness of 3½'.

The supply tank having been charged with sulphuric acid of 30° Baumé, and the acid heated by steam to from 87·5° to 100° C., the stopcock in the siphon is opened and kept so until the copper has become wetted throughout, after which it is closed and kept so for about 15 minutes (according to Bräuning, from ¾ to 1 hour), during which period, it is stated that, owing to the higher temperature in the interior of the vat, atmospheric air enters at the bottom of the vat, and ascends through the mass of granulated metal, whereby its oxidation is promoted. After the foregoing treatment the granulated copper, which at first appeared nearly black, owing to a coating of scale, will be found to have acquired a light brownish film; and on opening the stopcock a turbid, bluish-green, very acid solution of blue-vitriol will flow from the outlet at the bottom of the vat into the trough underneath. The blue-vitriol formed upon the copper during 15 minutes is effectually washed off by supplying hot acid to the vat, until it runs off clear, which occurs after the lapse of about 10 minutes. The process is thus continued until the whole of the copper has been converted into cupric sulphate. The object of this intermittent supply of acid is, it will be perceived, to facilitate the access of atmospheric air to the copper.

The length of the trough, which receives the acid, from the dissolving vats should be such that, after the hot liquor has circulated from one end of it to the other, its temperature may be reduced to that of the surrounding atmosphere, so as to cause it, in its course, to deposit on the bottom and sides of the trough, not only almost the whole of the cupric sulphate dissolved in it, but also the suspended particles of the precious metals. Before it reaches the furthest end

of the trough, from which it runs into the receiving tank, it should have become clear. The blue-vitriol is deposited in the state of small imperfectly formed crystals. From the receiving tank the clear liquor is raised by means of a kind of Giffard's injector, made of hard antimonial lead, into the supply tank, from which, after it has become heated, along with a due proportion of freshly added sulphuric acid, it pursues the same course as in the first instance; and so the process is repeated until the whole of the copper has been converted into sulphate. As solution proceeds fresh copper is added, so that practically there may be always the same mass of granulated metal in the vat. In each vat from 110 to 120 lbs. of copper are daily dissolved.

When the deposit of blue-vitriol, which is designated crude blue-vitriol (*Rohvitriol*), has accumulated in crusts of about 3″ thick on the bottom and sides of the trough, it is detached by means of copper chisels, and the pieces so separated are laid upon lead-covered floors, about 3′ broad, which adjoin, and are slightly inclined towards, the troughs. The thicker lumps are there broken into pieces and washed by sprinkling them with water, which removes adherent acid liquor, whereby, on recrystallization of the "crude" blue-vitriol, finer and deeper-coloured crystals are obtained, such as are sought for in commerce. [According to Bräuning, the "crude" blue-vitriol deposited nearest the dissolving vats contains most of the precious metals, and that nearest the receiving tanks contains more sulphate of lime and finely-divided arsenical and antimonial lead salts.]

In order to render the crude blue-vitriol marketable, and at the same time separate the intermixed precious metals, it is dissolved in the mother-liquor much diluted with water, and heated to 87·5° C. The solution is effected in leaden pans, 12′ long, 11′ wide, and 2½′ deep, which are heated by firing underneath. The pans are charged with about 200 cubic feet of liquor, and crude blue-vitriol is added until the solution, at the temperature above stated, marks 30° Baumé, dissolving being promoted by repeated stirring. When this stage has been reached, the pans, in order to prevent too rapid cooling, are covered with boards, and, without further firing, are left at rest for 12 hours, in order that the suspended particles of the precious metals, and the accompanying dirt and dust, the presence of which is almost inevitable, may have time to subside.

It happens occasionally that the solution contains some dissolved sulphate of silver; and when this occurs, it is necessary to precipitate the silver in the metallic state, which is done by adding to the solution a little very finely-divided copper, such as is formed in a certain degree by granulation, or, what is still better, copper scale (*Kupferhammerschlag*), which, consisting chiefly of cuprous oxide, is immediately converted by the free sulphuric acid, always present in the solution, into cupric sulphate and metallic copper in such a finely-divided state as to render it a particularly effective precipitant of silver. In order to obtain a clear solution of blue-vitriol and facilitate the recovery of the deposit of precious metals, the bottom of the

dissolving pan is inclined 4" downwards from one side to the other, and 4" above the bottom on the lower side there is a stopcock, by means of which the perfectly clear solution is drawn off into crystallizing pans. The small quantity of solution which remains in the dissolving pan is diluted with water, so that no crystals may form, and the diluted solution, together with the deposit, is run into settling vats. When the solution, after long standing, has become quite clear, it is carefully drawn off from the deposit by means of a siphon. The solution is used again for dissolving crude blue-vitriol; but the muddy residue is washed with water in order to free it as completely as possible from the larger particles of metallic copper, which may have been removed from the dissolving vats, and from any adherent solution. The washed residue is mixed with about 25% of litharge to the consistency of stiff paste, and formed into balls, which are dried and smelted; and the resulting lead, containing from 1·75% to 2% of precious metals, is cupelled. The proportion of gold is variable, but is never less than 1% of the silver.

The crystallizing tanks, which are made of wood and lined with sheet-lead, are 10' long, 5' wide, and 4' deep in the clear; and, in order to prevent loss of liquor, they are set on a floor, which is covered with sheet-lead, and slightly inclined towards a gutter communicating with a tank. Before filling these tanks with liquor, strips of lead are suspended within them, which reach nearly to the bottom, and the upper ends of which are fixed in holes in narrow pieces of wood laid across the tanks. Crystallization is completed in 12 or 14 days, according to the temperature of the surrounding atmosphere. The mother-liquor is drawn off, either by a siphon or through openings in the bottoms of the crystallizing vessels, into tanks, from which it is raised again by means of the injector into the dissolving pans, for the solution of a fresh quantity of crude blue-vitriol, or, if it has become very acid, into the tank, which receives the liquor from the crystallizing troughs. After the removal of the mother-liquor, beautiful large crystals of blue-vitriol are found adhering to the sides of the crystallizing tanks and to the suspended strips of lead, while there is deposited on the bottom a crust, generally somewhat thicker, of small crystals, which occasionally contain a little silver carried over from the dissolving pans, and have therefore to be redissolved. The good crystals of blue-vitriol are detached from the sides of the crystallizing tanks and the strips of lead, washed in cold water in order to remove adherent liquor and any dirt, and then spread on large boards in a heated chamber, where they are left until they have become thoroughly dry, without losing their water of crystallization, and, as a consequence, their beautiful colour.

RESULTS OF THE PROCESS.

At Oker, in 1870, during 350 working days, 402,600 lbs. of granulated copper were dissolved in 10 vats, with a consumption of 873,152 lbs. of sulphuric acid of 50° Baumé. For redissolving the resulting crude blue-vitriol there were 4 boiling pans, having an

ggregate available capacity of 800 cubic feet, and crystallizing anks of an aggregate available capacity of 9600 cubic feet. For ach boiling pan there were 12 crystallizing tanks, each of the apacity of 200 cubic feet. The quantity of good crystallized blue-itriol produced amounted to 1,531,877 lbs., or 2·87% less than is ndicated by the weight of the copper operated upon, a loss ascribed o impurities in the copper, of which oxygen generally constitutes ore than 1%,[2] the other impurities being foreign metals, slag, and urnace-bottom. In heating the dissolving pans and a boiler for roducing the steam required for raising the various liquors and eating the sulphuric acid, 1,043,300 lbs. of coal were consumed. In he treatment of the residues containing gold and silver, the loss of ead amounted to 8·4%; but, on the other hand, the silver obtained xceeded by 3·5% the amount which had been computed to be resent in the copper. It should be stated, in conclusion, that not nly does this process yield a larger proportion of silver than the ethod of liquation, but that this silver is also considerably richer n gold than that obtained by liquation. [According to Bräuning, centner of granulated copper yields 380 lbs. of blue-vitriol, with consumption of 240 lbs. of sulphuric acid of 50° B.; and from one ystem of 6 dissolving vats, 2 boiling pans, and 24 crystallizing vats, re obtained on the average from 25 to 30 centners of blue-vitriol in 4 hours.]

Extraction of Silver and Gold from Copper by Electrolysis.

Two patents have been granted to Mr. James Balleny Elkington, f Birmingham, for "Improvements in the Manufacture of Copper nd in separating other Metals therefrom" by electrolysis, the first n 1865[3] and the second in 1870.[4] In general outline the process is he same in both patents, and the claim in the second is solely for nprovements in the method of procedure. The following informa-on on the subject is derived from the specification of the second atent; and, with the exception of merely verbal alterations, it is resented in the same language as the original.

Copper ores are preferred which contain sufficient silver materially o injure (?) the copper if smelted in the ordinary way, and which, is asserted, would on that account be usually submitted to a esilverizing process previously to smelting. Although in such ores he quantity of silver is frequently insufficient to defray the cost f desilverization, yet the extraction of the silver is declared to be ecessary when copper of high quality is required. Ores of this ind are particularly suitable for the process in question, as the ilver which they contain does not raise their price in the market, nd can be recovered without any additional cost. Ores containing a

[2] It will be borne in mind that the copper treated is in the "dry" state, *i.e.* richly impregnated with cuprous oxide.

[3] No. 2838, Nov. 3rd, 1865.
[4] No. 3120, April 19th, 1870.

larger quantity of silver, say 8 ozs. per ton and upwards, and which are now always desilverized before being smelted, may also be profitably treated by this process; and so, indeed, may ores which contain little or no silver, the advantage in this case being mainly due to the better quality of the copper produced.

The ore is smelted "in the usual way, so as to obtain all its metallic contents (except such as may be volatile) in the form of regulus, from which stage by preference, *but it is not essential*, the metal is carried on to the state of pimple- or blister-copper." [Is it to be inferred, from the words which I have indicated by italics, that a regulus of copper may be directly used, instead of metallic copper, in this electrolytic process? If so, it is to be regretted that the patentee should have contented himself with the bare mention of a statement so remarkable!] This impure copper is cast into plates, say, 24″ long, 8″ wide, and 1″ thick; and in the centre of one end of each plate there is a stout T-shaped head of wrought copper, which is attached by placing it in the mould, so that the molten metal may flow round the lower part of the stem of the T. The metal is tapped out of the furnace on to a sand floor, and led by channels into the moulds, which are of cast-iron. The plates thus cast are ready to go to the dissolving house.

The floor of the dissolving house is laid with wood, and inclined, $\frac{1}{2}$ inch to the foot, from one end to the other. The boards are grooved on their edges, and small strips or tongues of wood are inserted in the grooves, so that there may be no open joints; and the surface is thoroughly saturated and coated with pitch, in order to make it watertight. The floor is divided from end to end into a number of troughs, formed by ledges of wood fixed down upon it, and which are also saturated with pitch. Each trough is wide enough to receive a row of three jars side by side, and is filled from end to end with jars. There may be about 12 troughs in the width of the building, and about 100 jars in each. There are gangways between the troughs for workmen engaged in the process.

The jars are cylindrical, 18″ in diameter and 34″ deep. They should be made of stoneware, which resists the action of the solution with which they are charged. [I believe there is no better ware for the purpose than that manufactured in Lambeth, which is glazed with salt, and known as Vauxhall stoneware.—J. P.] In each jar there are three holes, one in the bottom fitted with a wooden plug, a second in the side 4″ above the bottom, and a third 4″ below the top and diametrically opposite the second. The jars are made to stand vertically on the inclined floor by placing wooden wedges saturated with pitch under the bottom, and are connected together from the upper to the lower end of the room, each jar communicating with the next jar in the series by means of a pipe, one end of which is inserted in the opening near the top of the former, and the other in the opening near the bottom of the latter. The pipes may be of lead of about $\frac{1}{2}$ inch bore, and the connections with the jars are made of vulcanized india-rubber.

The solution which is used in the process is water saturated with cupric sulphate, which may be made either with the commercial salt, or by boiling in water the deposit found in the culvert or long flue conveying the smoke from the copper furnaces to a high chimney. The solution is stored in a tank at the upper end of the dissolving house, from which it flows into the uppermost jars, and thence from jar to jar until those at the lower end of the building are filled. Clips are put upon the india-rubber connections to stop the flow through the pipes when the jars are full, and so to keep the solution at the proper level in the upper jars.

When the process is in operation, the clips are taken off, say, once in 24 hours, so as to cause the solution to flow through all the jars; and as in working it tends to become weak at the top of the jars, its density is thereby equalized,—a point stated to be of great practical importance,—the stronger solution at the bottom of one jar flowing into the weaker at the top of the next jar, and so on in succession throughout the whole series of jars. At the lower end of the dissolving house the solution from the jars passes into a tank from which it is pumped back into that at the upper and opposite end of the building. There are two such receiving tanks at the lower end of the floor, so that there may be no interruption in the process when it is necessary to remove the sediment deposited from the solution in the manner stated hereafter. On the gangways between the troughs runs a truck to convey the copper plates to the dissolving jars. In each jar six of these plates are suspended in couples from copper bars placed horizontally, and having forks upon them to receive the T-formed heads of the plates. These bars rest at their ends on bars of wood laid on the jars, and extending across a row of three jars; and the same bars also support over each jar two metal cross-bars, from each of which are suspended two plates to receive the electro-deposited copper. The four receiving plates in each jar are interposed alternately between the cast-copper plates. Strips of sheet-copper are laid upon the wooden bars, so as to couple the cast-plates of one jar with the receiving plates of the next jar, and so on throughout the series of, say, 100 jars. Each metal cross-bar is made to bear on a connecting strip at one end, and at the other on a wooden block saturated with pitch. Each jar is provided with a false bottom of wood, to protect it from breakage in case a plate should fall. The receiving plates may be of wrought copper, but in the first instance gutta-percha coated with bronze powder is preferred. As soon as a sufficiently strong sheet of copper has been deposited, the gutta-percha is stripped off, and the sheet immersed in the solution.

A series of, say, 100 jars having been thus "coupled up into a circuit," the terminals of the series are connected with one or more electro-magnetic machines; and those used by the patentee are manufactured by H. Wilde and Co., of Manchester, and designated by them "three-and-half inch machines." They are driven at the rate of 2500 revolutions per minute; and with three such machines working into a series of 100 jars, 4 or 5 lbs. of copper may be deposited in 24 hours

in each jar without injury to the solution. When the cast-plates have become so much reduced as to be no longer fit for use, what remains of them, after having been washed in one of the tanks at the lower end of the dissolving house in order to detach any residue adherent to their surfaces, is melted and re-cast. The T-heads of wrought copper may be used an indefinite number of times, as they are protected from corrosion by coating their stems with wax.

The receiving plates are allowed to grow until they attain a convenient weight, when they may either be melted and cast into cakes and afterwards rolled in the usual manner, or sent directly into the market. The solution may be used for a very long time, loss by evaporation being supplied by the addition of water slightly acidulated with sulphuric acid; but ultimately it will become so charged with ferrous sulphate as to be unfit for further use. If, however, the plates be made of pimple- or blister-copper, not much iron will be found in the solution. The silver or other metals (excepting the iron) which the plates may have contained sinks to the bottom of the jars, and is there allowed to accumulate until it reaches the lower side hole. When this occurs the bottom plugs are taken out of all the jars of the series, and the contents washed out into the floor trough, whence they run into the tank at the lower end of the dissolving house, where the undissolved residue subsides. When a sufficient quantity of sediment has accumulated, the tank is pumped dry, the sediment removed, and subjected to a process by which the silver which it contains may be extracted; and while this is being done, the other tank is used for receiving the solution. Other metals which may be present may also be separated, should it be considered desirable. No particular method of extracting the silver from the sediment is specified by the patentee.

The special claims of the patentee are stated to be the following:—

I. The general arrangement of the dissolving house, with its inclined water-tight floor, draining into a tank at its lower end, and with the dissolving apparatus arranged thereon as above described.

II. The arrangement of the apparatus, so that a flow of the solution may be established from time to time from the bottom of one jar to the top of the next, whereby the solution may be prevented from settling into different layers of different strengths.

III. The use of a solution prepared by boiling and washing the deposit from the furnace culvert.

IV. "The smelting of ores containing 8 ozs. of silver or more to the ton of ore, so as to obtain the silver and copper in the metallic form and alloyed together, and then separating the metals by dissolving and redepositing the copper by means of electricity."

Mr. Elkington informed me in July 1878, that he had been working, on a limited scale, the process described in his patent No. 3120, since 1869, and had deposited, on an average, 6 tons of copper per week; that the copper was used for "high conductivity

graph wire, and for other purposes;" and that "the residues had n treated for silver and gold in the usual way."

It is hardly necessary to remark that the separation of silver and er metals from copper, on the principle adopted by Mr. J. B. ington in his patented "Invention," was well known long erior to the date of his patent; but if proof of the fact be re- red, it will be found in the following statement published about years ago.[5]

"Max, Prince of Leuchtenberg, has submitted to more accurate estigation the black precipitate which is formed at the anode positive pole) when blue-vitriol is decomposed by the galvanic rent; and which consists of sulphur, selenium (from the sulphuric d), arsenic, tin (partly from the solderings), gold, silver, copper iron, which, except in the cases mentioned, proceed from the per. On melting 22 lbs. of this precipitate with black-flux, were ained 8 lbs. of an alloy, which consisted of 90·2 per cent. of silver, of gold, 2·2 of platinum (which had previously escaped detec- n), and 2·8 of metals 'slaggable' on the cupel. Subsequently Prince subjected an average sample of this deposit to complete lysis, with the following results:—

COMPOSITION PER CENT. OF THE DEPOSIT.

Sand	1·90
Antimony	9·22
Tin	33·50
Arsenic	7·40
Platinum	0·44
Gold	0·98
Silver	4·54
Lead	0·15
Copper	9·24
Iron	0·30
Nickel	2·26
Cobalt	0·86
Vanadium	0·64
Sulphur	2·46
Selenium	1·27
Oxygen	24·82
	99·98"

Mr. Elkington's statement that "if the plates be made of pimple- blister-copper, not much iron will be found in the solution," gests the question, what other varieties of copper are likely to ld a larger quantity of iron? But no information, it is to be retted, is given on that point.

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[5] Jahresbericht (Liebig u. Kopp) für 7 u. 1848, published in 1849, p. 1022. | Extracted from Petersb. Acad. Bull. 6. p. 129; and 7. p. 218.

SILVER-SMELTING.

In silver-smelting, properly so called, lead is always used as the vehicle for collecting the silver, either throughout the entire process, or only in the latter stages of it. In the first case, the process is simply one of lead-smelting; but, in the second case, the silver is at first collected in a regulus consisting mainly of sulphide of iron or copper, or of both, and is afterwards separated from that regulus by means of lead, in the manner to be hereafter described, an alloy of silver and lead being obtained in either case from which the former is extracted by cupellation. Silver-smelting is, in fact, involved in Lead-smelting; and as this subject has been considered at great length in the Author's volume on the Metallurgy of Lead, it will only be necessary in this volume to describe certain processes of an exceptional character.

SMELTING OF ORE CONTAINING SILVER CHIEFLY IN THE METALLIC STATE.

SILVER-SMELTING AT KONGSBERG, IN NORWAY.

I am indebted to my friend the late David Forbes, F.R.S., for the following excellent description of the process of smelting at Kongsberg, in Norway, where the ore contains silver chiefly in the metallic state. Mr. Forbes was engaged during several years in the management of the Nickel Works at Espedal, established by the firm of Evans and Askin of Birmingham. For six months before leaving England for Norway, he was a guest in my house in Birmingham, where I then lived, and was occupied jointly with myself in analysing various crystallized slags. He was a very careful and persevering worker, and would, if his time had not been so largely occupied in professional engagements in the latter years of his comparatively short life, have added greatly to the number of his valuable contributions to the sciences of mineralogy, geology, and metallurgy. I should state that the description of the Kongsberg process was corrected when in type by Mr. Forbes.

The silver mines of Kongsberg, in Southern Norway, have been in uninterrupted and successful operation for more than two and a half centuries; and, notwithstanding that several of the workings have attained a depth of more than 300 fathoms from the surface, no signs of a cessation of metallic richness likely to discourage further explorations in depth have as yet (1874) been met with, although from the very commencement of the mining operations in 1624 the history of these mines presents a series of alternating epochs of extreme richness and poverty.

The lodes traverse the crystalline schists, and from the researches of Kjerulf and Dahll appear to be intimately connected with the intrusion of the eruptive Gabbro, which has broken through and disturbed these rocks.

The silver in the lodes is found principally as native silver along with more or less sulphide (silver-glance), both often in magnificent crystals; minute particles of pyrargyrite, stephanite, and fire-blende are occasionally met with; and horn-silver (kerargyrite) has been observed in the more superficial parts of the lodes. The other metallic compounds met with in the lodes (only in small quantity) are pyrrhotine, often finely crystallized, iron-pyrites, copper-pyrites, zinc-blende, galena, and chalybite; whilst the veinstone or gangue consists principally of calcite and quartz, with occasionally barytes, steatite, and some fluor-spar, prehnite, harmatome, and other zeolites. Anthracite in small nodules or fragments is not unfrequently found imbedded in the veinstone.

The native silver in most of the mines seldom contains any or only a mere trace of gold; in one of the ancient long-abandoned mines, however, a native alloy of silver and gold has been found and recently described by Hjortdahl. Whether in the crystalline or dendritic form, the Kongsberg silver appears invariably to contain mercury, in some cases amounting to as much as 2 per cent. of the silver. Scheerer also found in one specimen of native silver 0·7 per cent. of antimony, but could not detect any mercury in the silver-glance.

By far the greater part of the entire production of silver at Kongsberg is derived from the native silver, which often occurs in massive blocks weighing several hundred pounds. In 1847 I saw in one part of the mine a face of ore standing in the lode about 7 fathoms high by $\frac{3}{4}$ fathom wide, which literally was one mass of native silver, and estimated to be worth several million dollars.

The silver ores as they arrive from the mines are broken up and picked over by hand to separate the portions rich in visible silver; the rest is then crushed under light stamp-heads working in troughs without gratings, but provided with flushets, and the slime is then concentrated by the use of percussion tables.

The result of this treatment is to classify the dressed products under the following heads:—

a. Native or metallic silver, containing a little silver-glance and veinstone; it averages about 75 per cent. of fine silver, and is sent to the refinery to be treated as described under A.

b. Rich washed ores, containing about $\frac{1}{2}$ per cent. of silver, which are sent to the smelting for concentrated regulus, B 3.

c. Poor washed slimes, with from 15 to 20 ounces of silver to the ton of ore, which are sent to the ore-smelting operation, B 1.

d. Tailings with less than 4 ounces of silver to the ton, which are thrown into the river.

The smelting process will be described under two heads, namely, Silver-Refining and Ore-Smelting.[1]

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[1] The metallurgical treatment of the silver ores at Kongsberg has been much improved by Mr. Samuelson, who for many years has been and still (in 1874) is the manager of the smelting department of the Government works.

A. Silver-Refining.

This process is employed not only in the treatment of the native silver direct from the mines, but also of the coarse silver from the cupellation-hearth, after the treatment of the silver-lead produced in the various operations of the ore-smelting process.

The native silver direct from the mines or from the stamping-mill is received at the furnaces in the form of irregular fragments of all sizes; and as a large portion of it has been taken out of the stamp-boxes, where it has been left behind after all the matrix and finer particles have been carried off by the current of water, it usually presents itself as a mass of flattened-out metallic particles, often, as it were, felted together by the pounding action of the stamp-heads.

A 1. The refining takes place at the smelting works thirteen times each year—that is, once every mining or lunar month; the quantity operated upon each time being entirely dependent upon the amount of native silver which may have been received from the mines during the preceding month.

In this operation the native silver is placed upon the refining hearth or test along with a small quantity of wrought-iron clippings or iron wire (but when the rough silver from the cupellation-hearth is refined, no clippings or wire is added), in order to decompose any sulphide of silver which it may contain, and it is then covered, or rather sprinkled over, with about from 1 to 1½ per cent. of its weight of litharge; the furnace-doors being now closed, the silver is melted down rapidly by the flame of wood, and, when in perfect fusion, is freed by skimming from the impurities which float upon its surface, after which it is cast into bars. The products of this operation are as follow:—

a. Bar or fine silver, sent to the mint.
b. Skimmings, partly metallic and partly scoriaceous, which are re-smelted as described under A 2.
c. Condensing-chamber fume, removed once a year, and sent to B 5.

The furnace employed in this operation is not unlike an ordinary English cupelling or test furnace; but differs from that furnace in the manner in which the test is supported. The bed, or test, instead of resting upon fixed iron bearers, as in the English furnace, is supported upon a small iron framework or carriage running upon rails attached to the floor of the furnace-house; behind, the test rests upon a pair of trunnions, whilst in front it is held up by a simple mechanical arrangement of gearing, which, when the operation is concluded, allows the fore part of the test to be depressed and inclined gradually, so that the silver may run off at once into the ingot moulds.

The bed of the test is composed of an intimate mixture of five parts of powdered impure siliceous limestone and one part of ordinary clay. Crystalline limestone or marble has been tried, but not found suitable for this purpose.

Owing to the large quantity of native silver treated at one operation by this process (frequently as much as 2000 lbs. at a time), a considerable quantity of mercury is seen to be condensed in the form of globules in the cooler parts of the furnace; and it is probably owing to the volatilization of this mercury that the fume found in the condensing chambers attached to this furnace is so much richer in silver than that obtained from any of the other operations. On one occasion at which I was present the native silver refined yielded 88·78 per cent. of its weight of fine silver, but more generally 75 per cent. is nearer the average yield.

A 2. The skimmings from the refining are after each operation run down with charcoal in a miniature blast-furnace, about $2\frac{1}{2}$ feet in height, and the products of this fusion are as follow:—

a. Impure silver, containing about 80 per cent. of fine silver; this is added to the native silver to be refined in the next month's operation, A 1.

b. Silver-regulus, containing up to 10 per cent. of silver, sent to B 3: about a $\frac{1}{4}$ of a ton of this is obtained annually.

c. Slag, containing from 20 to 30 ounces of silver to the ton, which is added to the charge in regulus-smelting, B 3.

B. Ore-Smelting.

The chemical examination of the dressed silver ores from the Kongsberg mines shows that they essentially consist of a very small amount of silver, chiefly in the metallic state (along with a still smaller amount combined with sulphur, arsenic, and antimony), disseminated through a preponderatingly large mass of stony matter; and this fact has led to the adoption of a system of smelting peculiar to this locality.

Since no ores of lead (which could be utilized in extracting the silver according to the more usual methods of smelting) are found in this part of Norway, an addition of native sulphide of iron is employed in the smelting process, for the purpose of separating the silver and concentrating it in the form of an argentiferous sulphide of iron or regulus.

The pyrites employed for this purpose, mined in the vicinity, is both iron-pyrites and magnetic-pyrites, and besides traces of arsenic, cobalt and nickel, usually contains a small percentage of copper, which, by becoming concentrated in the successive operations, renders the treatment of these ores still more complicated by introducing the necessity for utilizing the argentiferous copper products obtained in the course of the smelting operations.

The smelting is conducted in charcoal blast-furnaces, of which the height is 14 feet from the twyer to the charging door. Their construction is very similar to that of the furnaces usually employed in Scandinavia and some parts of Germany for smelting copper and silver ores. At Kongsberg they are built of, and lined with, the ordinary gneissic rock of the district, and the flues from all the different

furnaces enter into a condensing chamber, in which the larger part of the silver, volatilized or carried off in suspension in the smoke, is collected.

The blast which is introduced into the furnace by two twyers, 1 inch in diameter, placed on a level in the back-wall of the furnace, is furnished by a cylinder-blowing engine worked by water-power; the pressure of the blast is $1\frac{3}{4}$ inch mercury,[2] and it enters the furnace at a temperature of about 370° Fahr., the air having been heated in its passage through copper air-heating twyer boxes of peculiar and very ingenious construction, the invention of Mr. Samuelson, the head of the smelting department at Kongsberg.

The various operations of the ore-smelting process will now be described in succession, commencing with

B 1. Smelting for coarse Regulus.

In this operation the poorest slimes from the stamping-mills, containing from 15 to 20 ounces of silver to the ton, are run down with pyrites, slag from the concentrated regulus-smelting and the lead-regulus desilverizing operations B 3, 5, and 7, which contains at the highest 5 ounces of silver to the ton, and the condensing-chamber fumes and furnace-returns[3] from the previous smelting. The relative proportions of these substances are varied according to the nature and richness of the ore; and, with respect to the amount of pyrites added, the rule is, to employ as much as will produce a regulus not containing more silver than about 80 ounces to the ton; experience having shown that if the regulus be richer, the slag produced along with it is not so clean or free from silver as it would otherwise be.

As an example, a smelting charge in actual practice was noted by me some years back to consist of the following percentage proportions given in round numbers:—

	Per cent.
Poor silver ores slimes	35
Iron-pyrites	15
Slag from smelting B 3	45
Furnace-returns and condensing-chamber fume from B 1	5
	100

Each blast-furnace runs down about 10 tons of such a mixture or charge in the twenty-four hours, and one barrel (8 cubic feet) of charcoal from spruce-fir and pine, weighing about 44 lbs., smelts from 186 to, at the highest, 214 lbs., or say about $4\frac{1}{2}$ times its weight of the charge. The products obtained from this smelting are as follow:—

[2] In 1847, when I first studied the Kongsberg silver-smelting, only 4 lines of mercurial pressure were employed; in 1850 Mr. Samuelson had increased the pressure to $1\frac{3}{4}$ inch; and I understand that he has lately been using 5-inch pressure with advantage. The blast was formerly warmed by a cast-iron tubular hot-air apparatus heated by [illegible] wood, but during the last ten years this has been abandoned in favour of the copper twyers here described.—D. F.

[3] By furnace-returns are understood the fragments of furnace-lining, [illegible] unclean slag, sweepings, [illegible] &c., from previous furnace operations.

a. Coarse regulus, containing from 60 to 100, and on the average 80, ounces of silver to the ton of regulus, which is sent to the roasting stalls, B 2.

b. Slag, containing from $\frac{5}{8}$ up, occasionally, to 2 ounces of silver per ton, but not averaging above 1 ounce per ton, which is thrown into the river as valueless.

c. Condensing-chamber fume, with about 20 ounces of silver per ton, which is returned to next smelting, B 1.

As a rule, it may be observed that the larger the sump or hearth of the blast-furnace is made, the cleaner is the slag; a result evidently due to the influence of the greater mass of molten matter permitting a more perfect subsidence or mechanical separation of the regulus from the slag. As soon as the "sump" of the furnace becomes filled with regulus, the blast is turned off and the furnace is tapped, the regulus being allowed to flow into a large hemispherical hole sunk in the earthen floor of the furnace-house (about $2\frac{1}{2}$ feet in diameter and $1\frac{1}{2}$ deep). As the molten regulus cools upon the surface, the crusts formed on the top are removed in succession by sticking an iron hook through them, and lifting them off in the form of cakes or discs about an inch in thickness, the operation being continued until the entire tapping has been so removed. The object of so doing is to enable the regulus, when cold, to be more easily broken up into small fragments than could be done if it had been cast into pigs or solidified *en masse*.

It may be remarked here that assays of the uppermost crust, when compared with those of the lowest or last portion remaining in the casting hole, and technically called the "king," show this latter to be considerably richer in silver than the former; a result which I have also found to occur in the case of copper- and nickel-regulus when similarly treated.

B 2. Roasting the coarse Regulus.

The discs or cakes of coarse regulus obtained in the preceding operation are broken up into pieces of about 1 inch cube and taken to the roasting stalls, which are merely rectangular spaces enclosed on three sides by stone walls, about 12 feet long by 8 feet in width and 4 feet in height. The broken regulus is heaped up on the top of a layer of split wood, which, upon being lighted, sets on fire the fragments of regulus in its vicinity, and, once lighted, the combustion communicates itself by degrees to all parts of the heap without requiring further addition of fuel. It is allowed to burn until it goes out of itself, care being taken to prevent the regulus, especially in its first roasting, from sintering or fusing together into hard masses.

As soon as the combustion ceases, the mass of, as yet, but very imperfectly-roasted regulus is picked over and transferred to the next succeeding stalls, where it is treated in precisely the same manner as before; and this operation is repeated until the whole has become thoroughly roasted and appears as a somewhat porous black mass, with little or no metallic lustre upon its freshly-broken surface. In

general this will require five or six roasting turns, sometimes more; after the first turn it is usual to assist the combustion by the addition of a little small or refuse charcoal, interstratified throughout the mass of half-roasted regulus.

Dense fumes of sulphurous acid are evolved during the operation, and the colder parts of the heaps are coated with sublimed sulphur, frequently containing selenium and tellurium; occasionally realgar shows itself as a bright red incrustation on the regulus.

From these roasting heaps fragments may be taken which show very distinctly the different stages of kernel-roasting, and occasionally I have picked out specimens which contain a central kernel quite loose in an external shell of oxidized regulus (almost pure magnetic oxide of iron); a result owing to the intermediate zone of sulphide having fused and run out from between the two. In these cases the copper always concentrates itself in the kernel, but as yet no investigations have been recorded to prove whether this is also the case with silver.

In the stalls it is common to find pieces of roasted regulus, the external surface of which is coated with a bright film of metallic silver, as if sublimed on to it from some volatile compound of silver; this, however, cannot be accepted as demonstrating that the silver has travelled outwards.

B 3. Smelting of the roasted coarse Regulus and Desilverization of the concentrated Regulus.

In this operation the richer washed ores, containing about half per cent. of silver, are smelted along with roasted coarse regulus, and to these are added the condensing-chamber fumes from the operations B 4, 5, 7, and 8, and the small quantity of slag from smelting the skimmings of the native silver refinery, as already described under A 2, which slag is not charged in at the top of the furnace, but is placed in the sump or hearth, where it readily melts and incorporates itself with the concentrated regulus already there. The whole is smelted in a furnace precisely similar to those used in the coarse regulus-smelting, and the concentrated regulus is tapped out into the hole, as before described. Instead, however, of taking it off in plates or discs, the regulus, whilst still molten, is desilverized by the addition of pigs of English lead, using the lead in the proportion of 6 cwt. of pig lead to every ton of regulus.[4] After being stirred well with an iron rod, the metallic lead is allowed to separate itself by its own weight, when it carries down with it the larger portion of the silver contained in the regulus, after which the regulus is taken off in discs, precisely as in the case of the coarse regulus. The products of this double operation are as follow:—

a. Silver-lead, containing about 5 per cent. of silver, sent to B 4.

b. Rich lead-regulus, with from $\frac{3}{4}$ to 1 per cent. of silver, which is desilverized in operation B 5.

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[4] This is an ancient process, designated in German "Einränkarbeit."

c. Condensing-chamber fume, with from 100 to 120 ounces of silver per ton, which is sent to B 7.

d. Slag, with about 5 ounces of silver per ton, sent to B 1.

e. "Bears" or metallic bottoms, always rich in silver up to 1½ per cent. of silver, which are sent to operation B 5.

This smelting does not differ materially from what has been described when treating of the coarse regulus: the slag, however, is much more basic (containing a very large percentage of oxide of iron); and, consequently, there is a great tendency towards reducing the oxide of iron, and thus forming "bears" at the bottom of the hearth, which often attain so great a size and become so firmly attached to the bottom and sides of the furnace as to prove most troublesome, and eventually to stop the working of the furnace.

This method of desilverizing the molten regulus, upon its being tapped from the furnace, by the addition of pig-lead, although not so perfect as when lead or lead-ores are added to the charge and passed through the furnace, is found, however, to be much more economical in practice, since the loss of lead in the slags and by volatilization is infinitely less.

The higher the temperature of the molten regulus at the moment of adding the lead, the more perfect will be the desilverization of the regulus, and the reverse. When, however, the temperature is very low, it has been found by experiment that lead rich in silver will even yield up a proportion of its silver to the regulus.

B 4. Cupellation of the Silver-lead.

The silver-lead obtained from the last operation, as well as from operations B 5, 7, and 8, is now cupelled in an ordinary German cupelling hearth, with movable dome; the bed is composed of a mixture, finely pulverized, of four parts of siliceous limestone and one part of ordinary stiff clay.

The blast which plays over the surface of the metallic bath, in order to oxidize the lead, is previously heated by passing through cast-iron tubes placed at the sides of the fire-grate, and is directed on to the bath at an angle of about 20°, through a flat nozzle shaped like a double loop ; but towards the end of the operation a smaller nozzle, of similar shape, is employed, and the angle of inclination is increased to about 30°.

From 3 to 3½ tons of silver-lead are thus cupelled at a time, and usually, towards the end of the operation, copious arsenical fumes are given off from the bath.

The products of the operation are—

a. Test-silver, sent to A 1.

b. Crude and clean litharge, containing about 7 ounces of silver per ton, sent to B 5.

c. Cupel bottom, and condensing-chamber fumes, containing from 20 to 30 ounces of silver per ton, also sent to B 5.

The loss of lead in this operation is stated to amount to about 6½ per cent., which will be about 1¼ lb. lead for each pound of silver.

B 5. Desilverization of the rich Lead-regulus.

This operation is conducted in a low blast-furnace, 4 feet in height, the regulus, without any preliminary treatment, being at once run down with charcoal along with from one-third to one-half its weight of a mixture of the litharge, broken test and cupellation bottoms from the operations A 1 and B 4, and the condensing fume from A. As the smelting proceeds, fragments of the metallic "bears" from the furnace-bottom, B 3, are added from time to time; they are easily absorbed and desilverized by this process.

The products of this smelting are—

a. Rich silver-lead, with from 2 to 2½ per cent. of silver, sent to B 4.

b. Condensing-chamber fume, sent to B 3.

c. Slag, containing about 3 ounces of silver per ton, sent to B 1.

d. Intermediate lead-regulus, containing from ⅜ to ½ per cent. of silver, which, without blowing out the furnace, is at once returned to it and treated exactly as before, with from one-third to half its weight of litharge and broken test and cupellation furnace bottoms.

After passing through the furnace, the products now are—

a. Poorer silver-lead, containing from 1 to 1¼ per cent. of silver, which is used along with English pig-lead for desilverizing the concentrated regulus, as described under B 3.

b. Slag, with about 3 ounces of silver to the ton, sent to B 1.

c. Condensing-chamber fume, sent to B 3.

d. Poor lead-regulus, sent to the roasting stalls, B 6.

B 6. Roasting of the poor Lead-regulus.

The regulus from the last operation, after having been broken up by hand to the size of about 1-inch cubes, is roasted in open stalls, precisely as described under B 2, and generally requires about four or five turnings.

B 7. Smelting and Desilverization of the roasted poor Lead-regulus.

The roasted regulus is smelted in a 14-feet high blast-furnace, precisely as described when treating of the smelting for concentrated regulus under B 3; but, owing to the small amount of copper originally present in the ore and in the pyrites added having now concentrated itself during the successive operations, the products are—

a. Rich copper-regulus, with from ¾ to 1 per cent. of silver, sent to B 8.

b. Silver-lead, with 5 per cent. of silver, sent to B 4.
c. Condensing-chamber fume, with from 100 to 120 ounces of silver per ton, sent to B 3.
d. Slag, with 5 ounces of silver to the ton, sent to B 1.

B 8. Desilverization of the rich Copper-regulus.

This operation is conducted in a low blast-furnace, with one twyer 4 feet in height, in exactly the same manner as when desilverizing the rich lead-regulus, B 5, the products obtained from the double operation being as follow :—

a. Rich silver-lead, containing from 2 to 2½ per cent. of silver, sent to be cupelled, B 4.
b. Poorer silver-lead, with from 1 to 1½ per cent. of silver, which is used along with the English pig-lead for desilverizing the concentrated regulus, B 3.
c. Condensing-chamber fume, which goes to B 3. Slag, with 3 ounces of silver to the ton, sent to B 1.
d. Poor copper-regulus.

The poor copper-regulus is broken up, roasted in stalls, and smelted in blast-furnaces for black-copper. This black-copper is subsequently liquated according to the old German system, and this operation is twice repeated; after which the copper is refined to cake-copper, which then still retains about 30 ounces of silver per ton of copper. The small amount of copper-regulus produced at the same time along with the black-copper is also desilverized in the same manner as described when treating of the desilverization of the rich copper-regulus, B 8.

Of late years Mr. Samuelson has tried, with success, instead of the liquation process, oxidation or scorification of the copper with lead in the ordinary cupellation hearth, with movable dome (employed in B 4). The cupriferous litharge was even more fusible than pure litharge, and it was found that six parts of lead would carry off one part of copper in the litharge.

The cupriferous litharge is subsequently employed in desilverizing the rich copper-regulus (B 8), in which operation the copper is again recovered, and goes into the poor copper-regulus.

The expense of smelting the silver ores at Kongsberg may be estimated from the statement of Mr. Samuelson, and the result is, that supposing no charge to be made for the ores delivered at the furnace, they can be worked without loss when they contain 0·4 loth per Cologne centner, *i.e.* = 0·0125 per cent. of silver, or 4 ozs. 1 dwt. 15 grs. per English statute ton.

A comparison of the yearly yield of silver with the produce of silver which, according to the assays, should be obtained, shows that the actual quantity extracted is slightly in excess of what it should be according to the assays.

The following table shows a summary of the different operations of the Kongsberg process in a concise form:—

KONGSBERG SILVER-SMELTING PROCESS.

SUMMARY OF OPERATIONS.

A

A 1. Refining Native and Cupellation Silver.

Products.

Skimmings treated by process	Condenser fume to B 3.	Bar silver to mint.

A 2. Skimming-Smelting.

Products.

Impure silver returned to A 1.	Slag to B 3.	Silver-regulus to B 3.

B

B 1. Smelting Ore for coarse Regulus.

Products.

Coarse regulus sent to roasting stalls for	Condenser fume to B 1.	Slag thrown away.

B 2. Roasting coarse Regulus,

and afterwards to

B 3. Smelting for concentrated Regulus.

Products.

Rich lead-regulus to	Silver-lead to	Metallic bears to B 5.	Slag to B 1.

B 5. Smelting and desilverizing of rich Lead-regulus.

Products.

Poor lead-regulus sent to roasting stalls for	Condenser fume to B 3.	Slag to B 1.	Poor silver-lead to B 3.	Rich silver-lead to B 4.

B 4. Cupellation.

Products.

Condenser fume and cupellation hearth bottoms to B 5.	Crude and pure litharge to B 5.	Cupellation silver to A 1.

B 6. Roasting of poor Lead-regulus,

and afterwards to

B 7. Smelting and desilverizing of poor Lead-regulus.

Products.

Silver-lead to B 4.	Condenser fume to B 3.	Rich copper-regulus to	Slag to B 1.

B 8. Desilverization of Copper-regulus.

Products.

Condenser fume to B 3.	Slag sent to B 1.	Poor copper-regulus, which is roasted and smelted for black-copper, which is afterwards liquated three times in succession, and then refined to cake copper.	Poor silver-lead to B 3.	Rich silver-lead to B 4.

Remarks on the Kongsberg Process by the Author.

In the first part of this process, or that which is described under the head of "Silver-Refining," the rich ore containing on the average 75 per cent. of silver, mostly in the metallic state, is simply melted in a shallow-bedded furnace with the addition of a little wrought-iron, which reduces any sulphide of silver that may be present, with the formation of sulphide of iron (see p. 30 antea). But a little litharge is afterwards added with the object of scorifying this sulphide of iron and any foreign matter existing in the ore, so that these impurities may be skimmed off in the state of slag.

This process, however, is not confined to the treatment of silver ore like the rich ore of Kongsberg, but has for more than two centuries at least been applied to rich ores in which the silver exists wholly in combination with sulphur or other so-called electro-negative elements; and, as will be shown hereafter, it is still in use in silver-smelting works in this kingdom. An excellent account of it, founded on his personal observation in Bolivia, was published by Alonzo Barba in 1640.[5] Fusion was effected in a reverberatory furnace on a bath of molten lead, containing usually 2 or $2\frac{1}{2}$ quintals to 1 quintal of rich ore. Barba gives precise directions for the management of the process, of which the following may be mentioned. When the molten lead has become bright and clean like quicksilver, and begins to waste (*gastar*, i.e. as the result of oxidation), a shovelful or two of the ore, in the state of small particles, is thrown on the top, care being taken that there should be only sufficient ore entirely to cover the surface of the lead, and that it should not be heaped up in any part. The bath should be constantly stirred with a hook or long stick, so as to bring every part of the ore in contact with the lead, and the stirring should be continued until the slag is uniformly melted and becomes as liquid as water. Fresh ore is to be added at intervals, giving it time to melt, and repeating the manipulation above described until the operation is completed. Very rich ore produces a small quantity of slag, but poorer ore much more. When much slag has accumulated in the furnace, it must be left to "boil and thoroughly liquefy" (*se dexe cocer, y sutilizar muy bien*), during which no ore is added. The slag is then to be tapped off, and, in order to lessen the risk of the escape of enriched lead at the same time, the surface of the bath need not be wholly freed from slag. A little of the lead is taken out of the bath with a ladle and assayed for silver, when, if it should be found that the weight of the lead does not exceed twice that of the silver, fresh lead must be put into the bath. The silver, it need hardly be stated, is finally extracted from the lead by cupellation.

Barba gives a clear description of his reverberatory furnace and illustrates its construction by engravings (probably in type-metal), which, though coarse and ill-drawn, are nevertheless quite intelligible;

[5] Arte de los Metales. Madrid, 1640. lib. iv. cap. 15 and 16.

whereas his French translator presents an engraving of this furnace, which is wholly unlike the original, and is quite unintelligible.[4]

The process described by Barba is a true scorification on a large scale, and the theory is precisely the same as that of scorification on the small scale (see p. 242 antea).

With regard to the second part of this process, or that which is described under the head of "Ore Smelting," several points deserve particular consideration. The first point to be noticed is, that, owing to the absence in the vicinity of Kongsberg of lead ores suitable for ordinary lead-smelting, the ore, which consists chiefly of stony or earthy matter so-called, with only a very small amount of silver, is smelted with the addition of iron-pyrites in order to produce a regulus of sulphide of iron in which the silver may be concentrated, and which may, therefore, be regarded as a substitute for metallic lead. The composition of the furnace-charge should be such as to form a well-melted slag, and a regulus not containing more silver on the average than about 80 ozs. to the ton, experience having shown that, when the regulus is richer in silver, the accompanying slag is not so *clean*, *i.e.* so free from silver, as it otherwise would be. The slag is thrown away, as it does not retain, on the average, more than 1 oz. of silver per ton.

The regulus consists mainly of sulphide of iron, but contains lead, copper, silver, probably antimony and arsenic, all in the state of sulphide. It is roasted and smelted in the manner described under B 3, p. 510, whereby a second regulus is produced much richer in silver than the first. This enrichment is mainly due to the action of the silica in the furnace-charge upon the oxide of iron generated in the operation of roasting, and the formation of ferrous silicate which passes into the slag. But this slag, it will be observed, is not *clean* enough to be thrown away, and must, therefore, be subjected to further treatment.

The second point in the Kongsberg process to which particular attention should be directed is the desilverization of the second or enriched regulus by means of metallic lead, in the manner described under B 3, p. 510. This is an ancient practice of which the process under consideration furnishes an excellent example. There are various modifications of it which will be described in the sequel. It is founded on the fact (see p. 32 antea) that, when sulphide of silver is heated with metallic lead in excess, it is reduced, though not completely, to the metallic state, its sulphur combining with one portion of the lead to form sulphide of lead, and its silver alloying with the other or unchanged portion; while there is no reaction between the lead and the sulphide of iron in the regulus. The extraction, however, of the silver from the regulus by this treatment at Kongsberg is far from perfect; for after desilverization the regulus retains as much as from $\frac{3}{4}$ to 1 per cent. of silver.

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[4] Métallurgie, ou l'Art de Tirer et de Purifier les Métaux. Traduite de l'Espagnol d'Alphonse Barba. 1752. 1.

he third point to be noticed in the Kongsberg process is the nent of the regulus after its desilverization by lead, which is ibed under B 5, p. 512. The regulus is smelted in a low blast- ce in admixture with substances containing oxide of lead and fragments of metallic iron. In this operation metallic lead is set and as it trickles down to the bottom of the furnace it seizes and s with any silver with which it may come in contact, whether silver be free or combined. The reduction of the lead may be ed by contact with the fuel or by the action of carbonic oxide, ie reaction which occurs when sulphide and oxide of lead are d together, and by contact with metallic iron. The desil- ation of argentiferous lead-regulus by such means has been considered in the Author's volume on the Metallurgy of Lead, what is there stated on the subject need not be repeated here. same remark also applies to the remaining part of the Kongsberg ss described at pp. 512 and 513. How copper becomes concen- d in the regulus by alternately roasting and smelting is ined under the head of "Lead-smelting at Freiberg" and else- e, in the above-mentioned volume of the Author.

LVER-SMELTING AT "THE WYANDOTTE SILVER-SMELTING AND REFINING WORKS," WYANDOTTE, MICHIGAN.

Nature of the Ore.

he ore is from the Silver Islet Mine, in Lake Superior, and has previously mentioned at pages 191 and 196 of this volume. It tremely rich and contains silver chiefly in the metallic state. vein was discovered by Mr. Thomas Macfarlane in a little rock he north shore of Lake Superior, now designated Silver Islet.[7] country rock is diorite in clay-slate, pieces of the former being sed in the ore. The native silver is generally disseminated igh the ore in more or less dendritic masses. The following rals have been observed in the ore or gangue:—Native silver, rm and massive,—cerargyrite (chloride of silver), where the rock been decomposed,—argentite, crystallized,—antimonial silver, es not determined,—niccolite (kupfernickel, arsenide of nickel hich cobalt has been detected),—annabergite (hydrous arseniate ckel, nickel-ochre),—galena,—blende (sulphide of zinc),—copper- es, crystallized, rare,—iron-pyrites,—marcasite (white iron- es),—gypsum,—calcite,—dolomite,—rhodocroisite (carbonate of anese),—quartz,—and graphite. As the vein runs under the r of the lake, ore is obtained that has been exposed to its action,

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he North Shore of Lake Superior lineral-bearing District. By W. M. is, M.E., Wyandotte, Mich. Febru- 877. Transactions of the American ute of Mining Engineers, 5. p. 481. a paper by the same author, read October 1873, "The Wyandotte Silver Smelting and Refining Works," in the same Transactions, 2. pp. 89–101. From the latter paper the information in the text is mainly derived.

both from the vein and as boulders, of which the gangue has become quite soft, and is usually stained green from the presence of nickel. The niccolite is so intimately mixed with native silver and sulphides that it is impossible to say whether the pure niccolite contains silver, but from the tests made it would seem that it does not.

At first the ore was divided into the four following classes:—I., containing from 2000 to 4000 ozs. of silver per ton (of 2000 lbs.), or from 7% to 14%,—II., containing from 600 to 2000 ozs., or from 2% to 7%,—III., containing above 100 ozs., or 0·3428%,—and IV., the waste of the mine, containing on the average 40 ozs., or 0·14%. The last class forms the larger part of the ore, which was not the subject of treatment, but which it was proposed to concentrate or amalgamate as might prove most profitable. In 1873, to which the following description applies, only two classes of ore were made, containing on the average from 900 to 1000 ozs., and waste (No. IV.).

Smelting Establishment.

A large outlay seems to have been incurred in plant, as may be inferred from the following details. The works comprise three stone buildings, [each?] 150′ long by 47′ and 50′ wide. The first contains the offices, laboratories, engine, and boiler, a No. 2 Root's blower, a No. 8 Blake's pump, crushing-room with Blake's crusher and two 30-inch mills, Dodge's pan-amalgamator and settler, used only for experiments at the time. The second building contains the refining-room with seven wind-refining furnaces, the cupelling-room with seven large English cupelling-furnaces, the bottom-room where the tests are prepared, the smelting-room and charging-floors with a block of four low blast-furnaces (*Krummöfen*) and two reverberatories, and a blacksmith's and carpenter's shop at the end of the building: in connection with the blast-furnaces is a flue-chamber about 150′ long and 4′ square. The third building contains two cupelling-furnaces, and the plant for desilverization by zinc with the furnaces for refining 25 tons of bullion daily. It was moreover proposed to add a nickel-refinery to these works.

Before proceeding to describe the process conducted at these works, which, it is reasonable to suppose, would not have been constructed on so extensive a scale if the proprietors had not calculated on a large and lasting return from the capital invested, it may be well, by way of warning to enthusiastic adventurers, to communicate the following information on the authority of the author of the paper from which the preceding account, dated October 1873, is extracted. In a second paper, read before the American Institute of Mining Engineers in February 1877, Mr. Courtis thus writes: "Mr. Macfarlane, unable to get the Canadians to raise the necessary money to carry on the work, in spite of the fact that many thousand dollars' worth of ore had been taken out, succeeded in interesting parties from the States. These parties bought all the lands of the Montreal Mining Company, and a capital of $73,000 paid a dividend

of $160,000 the first year, besides paying about $200,000 towards settlement with the Montreal Mining Company, and expending also a large amount of money to establish the plant.

"In the report for this year we find that the total amount of dividends has been $622,666·66, and the total production $2,237,479·84. The great outlay was needed at the mine to establish a town on a barren rocky shore; to maintain a foothold on a little rock not 80 feet square against the mighty storms of Lake Superior; to furnish steam-tugs, engines, pumps; and build a mill capable of concentrating over 75 tons of rock per day.

"Silver Islet stands to-day perfectly equipped for mining, concentrating, and smelting 50 to 100 tons of ore per day. It has immense tracts of land in a mineral district that has hardly been explored as yet. It has nearly $700,000 worth of property on hand and only $400,000 indebtedness, and its own vein has been exposed only about 800 feet deep and 600 feet horizontally. Yet to-day its stock is almost valueless. *The cause of this has been the failure to find a second pocket of ore in depth that promises returns.* [The italics are mine.—J. P.] Small amounts of ore have been found by the drill at different depths. It is the present intention to push the deep shaft 400 feet deeper and explore to the southward, which is the supposed direction of the dip of the silver bodies.

"The failure of Silver Islet to produce even expenses for the last two years has dampened (*sic*) the ardour of other mining companies, so that with the exception of very feeble efforts at other points, except Duncan, the results of whose development all interested are watching, there is no extensve mining being done.

"The average assay of all ore smelted from Silver Islet during the first three years was above 900 ozs. per ton. It is difficult to come down from the meteoric splendour of Silver Islet to chronicle failures at other points, but such must be the case."

"Meteoric splendour" is a happy expression, but whether Mr. Courtis be correct in not supposing "that Silver Islet is something unique, where there are so many good indications," the future alone will decide.

Process of Smelting.

Furnaces.—Small rectangular blast-furnaces made of fire-brick, with generally a single twyer, are used, and their dimensions are as follow:—3′ 3″ from front to back, 1′ 9″ wide at the twyer and a few inches wider at the top, and 4′ from the twyer to the top and 1′ 3″ from the twyer to the bed which slopes downwards to the tap-hole. Water-backs, and subsequently water-blocks at the sides, have been tried with apparent advantage on the score of economy. When the sides are of brick, they are so much cut away after the lapse of 4 or 5 weeks, the usual period of a campaign, as to necessitate greatly increased care in the working of the furnace. The bed consists of $\frac{3}{5}$ of coke and $\frac{2}{5}$ of fire-clay, by measure, which are ground together

in a mill until the mixture becomes as fine as flour: such a mixture, it is stated, forms a better bottom than one of coarser grain, as it does not absorb so much lead, and, if moistened just enough, will not crack.

At one time the height of the furnace was increased to 16 feet, and two twyers were used; "but," it is said, "owing to want of ore and other circumstances, it was changed back, though the running was quite successful." It is to be regretted that these "other circumstances" are not specified.

Smelting Mixture.—This mixture is composed of ore, galena, roasted regulus and slag from ore-smelting, leady and argentiferous products (old tests, refining ashes, sweepings, etc.), and fluxes. Only enough galena is used to furnish sufficient sulphur for a fluid regulus.[8] The fluxes are limestone and iron cinder from rolling-mills, or iron blast-furnace cinder, when a siliceous slag is required. It is stated that the mill-furnace cinder contained 75·06% of ferric oxide, which is certainly a mistake, as this cinder consists chiefly of ferrous silicate; and that the blast-furnace cinder contained 5·69% of ferric oxide, which is equally a mistake. But these mistakes are, probably, only typographical, as formulæ for these slags are appended, in which the iron is rightly stated to exist as ferrous silicate.

Five analyses, so called, are given of the ore mixture prepared for smelting; but they are so incomplete and unsatisfactory as to be useless either in a scientific or practical point of view, in proof of which the two showing the largest number of constituents are here inserted:—

Analyses.

	I.		II.
Carbonate of lime	7·57		22·90
Carbonate of magnesia	6·94		7·73
Alumina	—		3·84
Sesquioxide of iron	1·88		
Lead	40·24		0·80
Zinc	2·27		—
Silver	8·30		0·1445
Sulphur	3·36		0·64
Silicates	13·23		33·78
	83·79		69·8345

These analyses and others to be subsequently introduced were made by Dr. H. C. Hahn, chemist to the works.

I. In this mixture the ore was No. I. (see the classification of ores antea).

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[8] The lead ores used for mixing have been pure galena, argentiferous galenas from Colorado, and ores from Little Cottonwood, Utah, the latter being the most satisfactory. Colorado ores generally contain too much zinc to be used in large quantities with rich ores.

II. In this mixture the ore was No. IV. or "mine-waste."

The ore and flux are made up into charges of about 6 tons, each charge being intended for 24 hours' smelting. The amount of lead in each charge is so arranged that 1 lb. of the resulting argentiferous lead will contain 1 oz. of silver, or between 6% and 7%. The fluxes are added in such proportion as to produce a basic slag, in which iron predominates; and when the ore is running siliceous, enough lime is supplied to keep the specific gravity of the slag so low that the regulus may separate perfectly from it. About 10% of ore-furnace slag is added, partly to work up any rich or unclean slag, "but especially to make the charge more fusible." Roasted regulus, as well as iron cinder, is used to make a fluid slag and throw down the lead from the galena; and it is asserted that "experience shows that a mixture of both in a charge gives better results and a cleaner slag than either alone."

Fuel.—The fuel which has been used is coke from Hammondville and Connellsville, and that produced in the Detroit Gas Works; and with 1 ton of each of those varieties of coke the quantities of ore smelted were 0·83, 1·27, and 1·20 ton, respectively.

Quantity of Ore smelted daily.—The largest quantity of Silver Islet ore passed through a small furnace, such as that above described, is 2·7 tons; but the average is about 2 tons, owing to lead ores being used instead of litharge.

Products of Smelting.—The products are argentiferous lead, regulus more or less impregnated with nickel speise, and slag. The lead contains from 6% to 8% of silver, and is directly cupelled. Silver also, crystallized in octahedra and nearly pure, is often found filling little cavities in the inner part of the brickwork. To have the furnace work well a cake of regulus, at least 2″ thick, should be produced at each tapping; a statement not particularly instructive, because, of itself, it furnishes no indication as to weight. When iron cinder alone is used, the regulus becomes thick and spongy, and incloses shots of lead. The regulus is roasted in heaps, and used over again until the resulting regulus contains so much nickel that it can be worked for speise in the reverberatory furnace. During the roasting there is, it is stated, a partial sweating out of the speise, so that the lumps which are melted together contain a larger percentage of nickel than the other and better roasted part of the regulus. These lumps are picked out to be treated for nickel. The slags generally contain less than 5 ozs. of silver (per ton of 2000 lbs.), sometimes less than 1 oz., and less than 1% of lead. The small percentage of lead in the slag will probably surprise British and other European smelters. But what is more remarkable, two complete analyses of slag from smelting in the small furnace are given, in which lead does not even appear amongst the constituents. In order not to risk the charge of misquotation, these analyses are here presented:—

ANALYSES OF SLAG.

	I.	II.
Lime	10·77	15·88
Magnesia	1·97	3·39
Alumina	12·25	9·56
Protoxide of iron	41·11	33·80
Silver	0·017	0·026
Silica	33·77	37·13
	99·887	99·786

It is asserted that "if the charges are put up so that the slag will be very poor in silver, the loss in labour and fuel more than balances the saving in silver." The slag is thrown away, except what is wanted for flux, or what is too rich in silver to be rejected.

FLUE-DUST.—The flue-dust collected in the chambers amounts to about $\frac{1}{2}\%$ of the material smelted. The largest and richest part settles in the first chamber, and contains more than 3 times as much silver as that from the chimney. The two following analyses of the flue-dust are given:—

COMPOSITION OF FLUE-DUST.

	I.	II.
Lime	8·74	6·62
Magnesia	3·66	0·00
Alumina and sesquioxide of iron	14·43	18·54
Protoxide of nickel	0·08	
Protoxide of cobalt	0·09	trace
Oxide of zinc	6·23	
Protoxide of lead	19·91	23·77
Silver	0·286	0·292
Sulphuric acid	9·30	8·85
Silica	16·11	13·06
Carbonic acid and water	1·28	3·76
Insoluble matter, coke, etc.	19·13	22·14
	99·246	97·032

The flue-dust is mixed with lime-water to a paste, dried, broken up, and smelted along with the ore-mixture.

CUPELLATION.—The argentiferous lead is cupelled in an English cupellation-furnace on a test in which a mixture of 3 parts [by measure?] of ground limestone and 1 of fire-clay is substituted for bone-ash. The mixture is moistened with water, and in that state is stamped into the test-ring. A test, when full, holds about 650 lbs. (avoirdupois) of silver; but cupellation ends when about 3 or 4 tons of argentiferous lead have been worked off and the silver amounts to about 500 lbs., which operation requires 3 days, and is attended with a consumption of 1350 lbs. of coal per ton. In an ordinary English cupellation-furnace from 20 to 25 tons (of 2240 lbs. avoirdupois) of argentiferous lead may be worked off per week of 6 days, though in some works not more than 12 tons are worked off during that

d; and at one establishment in Wales the consumption of coal 10 cwt. per ton of lead.[9] Hence it will be seen, that at the ndotte Smelting Company's works considerably less lead was daily ed off than in British works where the smallest quantity is ed per day, namely, 2 statute tons of 2240 lbs., instead of only 1 3 ton of 2000 lbs. as at the above-named establishment. But this sily explained by the fact mentioned by Mr. Courtis; namely, that of the workmen had had any previous experience in cupellation. he two following analyses are given of what is designated de silver," by which, it may be inferred, is meant the silver as mes from the test:—

Composition of Crude Silver.

	Per 1000 parts. I.	II.
Iron	0·090	0·031
Nickel and cobalt	0·004	0·008
Copper	0·117	0·106
Bismuth	0·0058	—
Lead	1·090	0·260
Gold	0·0023	0·0015
Antimony	trace	—
Arsenic	—	—
	1·309	0·407
Silver	998·691	999·593
	1000·000	1000 000

he "crude silver" is melted in plumbago crucibles with the ion of sand, which is termed "refining," and melted into bars hing 450 ozs. each. The fineness of these bars is 999, and rally 999·5 by United States Mint assay, the latter fineness g, it will be seen, the same as that of the "crude silver" in II. analysis!

he slag produced in "refining" is stated to consist chiefly of te of lead, and the proportions per cent. of other ingredients ch a slag have been found by analysis to be as follow:—

Protoxides of nickel and cobalt	0·550
Protoxide of copper (CuO [idem])	0·203
Oxide of bismuth (BiO^3 [Bi^2O^3])	0·026
Oxide of antimony (SbO^4 [Sb^2O^4])	0·639
Arsenious acid	0·005
Silver	1·837
	3·260

ickel and Cobalt.—These metals are stated to be found in all roducts, especially in a green coating that covers the tests. The

[9] The Metallurgy of Lead, by the Author, p. 184.

nickel contained in the ore accumulates in the regulus, and the per centage increases each time the roasted regulus goes through the low furnace; and when it reaches about 14%, the regulus begins to assume the appearance of speise. It is then smelted in a reverberatory furnace with screenings from the roast-heaps, which contain a good deal of arsenic, sulphuretted lead ores, and siliceous chimney-slag or other material, in order to remove the oxide of iron in the state of ferrous silicate. A speise is thus produced which contains 25% of nickel. Hahn has determined the proportions per cent. of several of the ingredients in samples of regulus after successive roastings and smeltings in the low furnace, and the results are as under :—

	I.	II.	III.
Nickel, cobalt, zinc....	1·57	7·32	10·44
Lead.....	8·17	9·66	3·75
Copper.....	—	—	0·89
Silver.....	0·5954	0·5044	0·852
Sulphur.....	16·83	11·48	17·55
Antimony.....	—	2·38	trace
Arsenic.....	—	—	4·18
Slag.....	—	—	4·75

The specific of No. I., at 17·8° C., was 6·0672; and of No. II. at 18·3° C., 6·1086.

The separation of nickel in the state of arsenide or speise from the roasted regulus containing oxide of iron, by the action of silica and the formation of ferrous silicate, is, *mutatis mutandis*, precisely analogous to what occurs when a mixture containing copper, iron, oxygen, sulphur, and silica is strongly heated, arsenic in the case of nickel acting like sulphur in that of copper.

Note.—My friend Dr. Sterry Hunt has informed me (Oct. 28, 1878) that another large mass of ore is said to have been recently discovered at Silver Islet, and to yield $6000 of silver weekly.

COMBINED SILVER- AND LEAD-SMELTING.

SILVER-SMELTING IN ENGLAND AND WALES.

Great Britain and Ireland produce no silver ores, strictly so-called, worthy of particular mention; but foreign silver ores, chiefly from South America, have been largely imported and smelted, or otherwise treated, in this country during the last 40 years or more. The earliest smelters of these ores were, if I mistake not, the firms of Lucas, at Sheffield, and Sims, Wylliams, Nevill & Co., at Llanelly in Carmarthenshire. Smelting was effected in reverberatory furnaces, either in conjunction with lead ores or rich lead slags, or a mixture of both. At first, in the absence of much competition, the business appears to have been very profitable, as may be inferred from the fact communicated to me on authority many years ago, that not more than 2*s.* 6*d.* was paid per ounce of silver in the ore!

These ores vary considerably in mineralogical characters, and may contain native silver, simple or complex sulphides of silver, such as

rargyrite and proustite, chloride or chloro-bromide of silver, etc. t however variable in this respect, they are, when smelted, ›jected to essentially the same method of treatment.

For the following general description of the smelting of silver ores m indebted to my friend Mr. Allan Dick, who during about twenty ırs had charge of the smelting department of one of the largest rks in this kingdom.

CONTENT OF SILVER IN THE ORES.—The smelting of imported silver s in reverberatory furnaces with lead is largely carried on at sent in England and Wales. These ores contain on an average m 250 to 300 ounces of silver per ton; but some lots contain little as 50, and others, generally small ones, as much as 3000 or 00 ounces per ton of 20 cwt.

TREATMENT OF VERY RICH ORES.—The very rich ores are generally ated by *scorification* on a bath of lead in an ordinary *test*, after it s been used some time in making litharge, and when it is nearly rn out. It is patched up and left half full of rich lead, or rich d is put into it. The rich ore is then spread upon the lead to a pth of an inch or two, often mixed with rich litharge or refinery eepings rich in lead. After roasting and scorification has proceeded one or two hours, with occasional rabbling towards the end of e operation, the charge is raked off in a pasty state, and sent to the ixing-shed to be worked along with the average ores. The greater rt of the silver remains with the metallic lead. The process is peated till the lot is finished. If the lot be a large one, the lead tapped from time to time, and may contain several thousand ounces silver per ton.

PREPARING THE CHARGE OF AVERAGE ORES.—The average ores, from many mines and of as many different kinds as possible, are ranged near the mixing-shed, in the centre of the ceiling of which ere is a rose-jet, from which a fine spray of water can be made cover a space of about 3 yards in diameter on the floor. Inside e shed, round the walls, are various heaps of "grey-slag" from e smelting of argentiferous lead ores, "burnt pyrites" (containg a little copper if it can be got for nothing), old silver-ore *ds*, silver-ore residues of different sorts, fluor-spar, anthracite, and immings from the *richest* pots of Pattinson's process. These subances are previously crushed under heavy edge-runners to such a ate that they would pass through a sieve of ¼-inch mesh, but they e not sifted, owing to the generally poisonous nature of the dust.

A layer of grey-slag an inch or two thick is spread on the floor, er it a layer of silver ores, burnt pyrites or oxide of iron in some ate, and the other substances mentioned above, so that the mixture ien smelted may produce lead containing from 500 to 800 ozs. of ver per ton. These materials are all raked together with a long-›thed rake under the falling spray of water, to keep down dust d prevent the ore being carried away afterwards by the draught the furnace.

The mixture varies in different works, and even in the same

works at different times. On an average it may be said that imported ores require their own weight of slag, containing about 40% of lead, about 10% of their weight of anthracite (*culm*), 10% or 15% of burnt pyrites, 8% or 10% of skimmings from rich Pattinson pots (consisting principally of finely-divided lead coated with oxide), and fluor-spar in proportion to the old tests—say 5% to 10%.

The ores are used just as they are sold; but if any lot consists almost entirely of blende, it is generally calcined before being added to the mixture, or it is used in very small quantity. Otherwise chlorides, sulphides, arsenides, and other descriptions of ore are taken as they come.

Training of the smelters.—The best smelters are those who have been "brought up" to their work. They begin about twelve or thirteen years of age, assisting the bricklayers, buddlers, labourers, etc. As they grow older and stronger they take their part in the general routine of large smelting-works. From time to time they do the work of a smelter who may be sick or absent, but always under the guidance of an experienced workman. As a rule, they cannot stand regular furnace-work, especially night-work, till they are over twenty years of age. By that time they have assisted at the building, repairs, and pulling down of many furnaces fitted with different kinds of fire-places, hearths, flues, chimneys, etc. They have also assisted in the working of these furnaces, the construction of which they understand. They know how to manage fires, and they can deal with large quantities of molten matter. If naturally observant, strong, and handy, they become first-class smelters. They then earn about 25*s.* per week for twelve hours' work by day one week, and twelve hours by night the following week. The work goes on generally by 12-hour shifts; but where the men have "Unions" and have got the better of the masters, the work goes on by 8-hour shifts for twelve hours' pay.

Furnaces used.—The exact dimensions of the furnaces vary in different, and even in the same, smelting-works; but a furnace is generally selected which is large enough for the work of four men, two by day and two by night, the smelter working "in front" of the furnace, and his assistant "behind" or "at the back." Four smelters will cheerfully take in hand the working of such a furnace as is shown in figs. 82 and 83, and which is described in the Author's volume on the Metallurgy of Lead. It will not matter if the bed is two or three feet shorter and proportionately broader. The fire-place may be half the depth and proportionately longer and narrower; it may have either a common or a *clinker* grate. There may be one, two, or three doors on each side. Two is a convenient number, as they may be made large enough to enable the smelter to put in masses of slag, scrap-iron, etc. The arrangements outside the furnace shown in fig. 83 are satisfactory; but a notch should be shown cut in the pot close to the pit *a*, because it is through this hole that the smelter taps the regulus or lead, should there be risk of its going to the pit *b*. The notch is semicircular, about an inch and

a half deep; whilst open, it is evident that no regulus or lead can flow to *b*: it must flow out to *a*. There is generally a corresponding notch in the ring above, so that, when in position and plastered up with clay, as it is when in use, the smelter has command of a tap-hole at *a* which he can open or shut during the tapping of the furnace, to suit the quantity of lead, regulus, or speise which he sees coming from the furnace. It is often not used, and is always closed

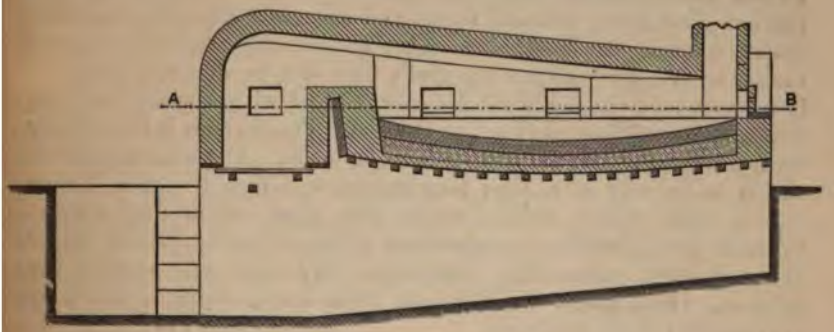

Fig. 82. Vertical section of the flowing furnace.

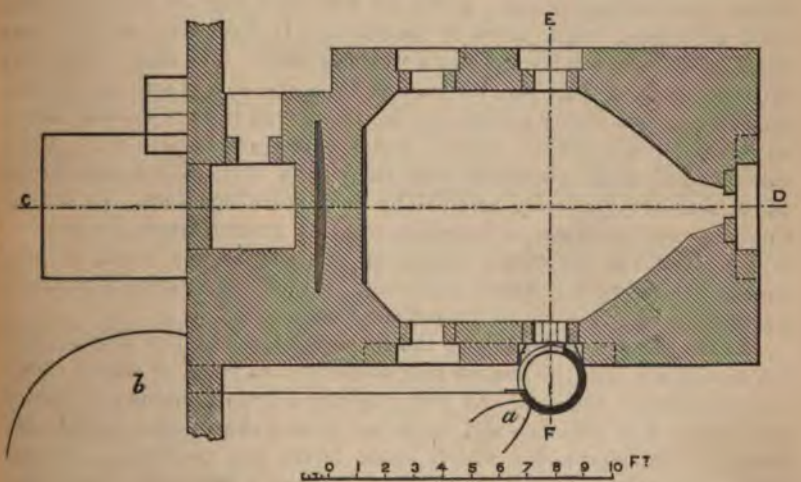

Fig. 83. Horizontal section of the flowing furnace.

when slag begins to flow through it. The slag then fills the remaining inch and a half of the pot, and afterwards overflows towards *b*. The cake of slag remaining on the "metal" in the pot is called the *kettle-piece*. It is always thrown back into the furnace because it is liable to contain "metal"—*i.e.*, lead, regulus, or speise.

PREPARATION OF THE FURNACE BOTTOM.—When such a furnace has been constructed for the first time, it is dried by a slow fire, during

about a week, after which the damper is raised higher and higher from time to time during about twenty-four hours, more and more fuel being thrown upon the fire. The smelters then take the furnace in hand, and the real work, so far as they are concerned, begins. They urge the fire and observe its action. Perhaps the heat is too much developed in the fire-place, or at one or other side of the interior, or it may be "swallowed"—*i.e.*, leaving the furnace almost untouched, and yet melting the interior of the flue. By means of bricks of different forms and sizes, and fire-clay, variously disposed about the fire-bridge and flue-hole, the smelters turn the tongue of fire, issuing from the grate, from side to side, and lengthen it or shorten it, till the whole interior is filled with a scorching fire, which dies away just as it enters the flue. The furnace is then ready for the slag of which the bottom is to be made. Any slag is selected which melts only at a high temperature and then becomes a thin liquid. Slag which softens easily like glass, continuing viscous through a long range of temperature before becoming liquid, is, for many reasons, unsuitable. Otherwise, any slag will answer the purpose. Good slags are obtained from iron-, copper-, lead-, or previous silver-ore, smelting.

During the firing of the furnace by the smelters, their assistants have been wheeling in some tons of suitable slag and heaping it under the working doors. Three or four tons will be required for such a furnace, much more if the furnace is built over an arch as usual, and if the smelters prefer a "strong bed." The slag is thrown into the furnace from time to time as it melts, and when the whole quantity is thoroughly melted the fire is allowed to burn down. The working doors are then opened and the damper is left up. The smelters and their assistants then strip for a turn of hot and hard work, and are generally assisted by four other smelters. In large smelting-works assistance is seldom wanting at such times, the bricklayers, even the labourers, taking an interest in the work, as all men do whose work is worth anything. Whilst the furnace is cooling a little, the smiths come to inspect the "clamping."

As the sides, and bottom of the furnace adjoining the sides, cool, the smelters splash the molten slag towards that point at which they wish to thicken the bed. At every splash a little remains adherent, until by dint of patience and continued labour the furnace bottom is brought into shape, for which some hours are required. When finished, the tap-hole is broken open. To enable this to be done more easily, it is guarded by a lining of sand or dry lime covered with clay before the slag is melted, and this lining is so placed as to protect the *tap-hole jambs*. The furnace is thus left to cool slowly during forty-eight hours or thereabouts, the damper being kept down.

First charging and management of the furnace.—The regular work of the furnace is begun by urging the heat to the utmost, in order to melt the surface of the bed, and enable the smelter to judge of the working of the fire now that the furnace is complete. The first charge of 30 cwt., or thereabouts, of the mixture

containing silver-ore is then thrown into the furnace and spread more thickly where the heat will be greatest. None of the charge is allowed to rest upon the lowest part of the bed near the tap-hole. About ¾ cwt. of "scrap" cast-iron is arranged inside around the tap-hole cavity. The doors are plastered up, the pot filled with argentiferous lead, and the charge gradually melted down. It is then tapped. Little or no lead or *slurry* (sulphides and arsenides) comes from the first few charges. The "metal" is absorbed into the furnace bottom or works its way outside and around the pot, and is not recovered till the furnace is finally pulled down.

Assuming the furnace to be in regular working order and that a charge has just been tapped, the smelter and his assistant having opened the working-doors proceed as follows with the next charge.

PREPARATION OF THE FURNACE FOR THE NEXT CHARGE.—The bed of the furnace is scraped to detach any lumps of clay, bits of brick, or portions of the previous charge which may have remained unmelted. The sides and bed are "fettled" if need be. The *tap-cavity* is "dried up" with lime or crushed old refinery *tests* containing lead and silver. The term *tap-hole* is generally applied not only to the hole through which the charge is tapped, but to all the lower part of the bed in front of which the *tap-hole jambs* stand. To prevent misunderstanding it seems convenient in this description to introduce some term to distinguish the space between the tap-hole jambs, through which space the charge is actually tapped from the cavity or well within the furnace which contains the molten mass. By way of distinction the former will therefore be called the *tap-hole* and the latter the *tap-cavity*. The smelter having "dried up" the *tap-cavity*, proceeds to detach any slag, regulus, or metal adherent to the *tap-hole*, and prepares it for the lump of clay with which it is to be filled.

REGULAR COURSE OF CHARGING AND WORKING.—The charge is then thrown into the furnace or dropped from the hopper. The "kettle-piece" from the preceding charge is next thrown into the furnace towards the fire-bridge, and the skimmings from the same charge towards the flue. The tap-cavity is cleared of any lumps which may have rolled down, and the scrap-iron is arranged round it. The tap-hole is again fettled, if need be, and a large lump of wet clay thrust into it so as to go in part well into the furnace. The lump is held in position by the smelter, whilst his partner from the back of the furnace presses a long-handled tool against it, working it well towards the jambs. The working-doors are then plastered up and the charge is left "to warm." For this there generally remains enough fuel in the grate from the previous charge, but, if need be, a little fuel is added, and the whole is left with the damper down for about two hours. After the kettle-piece has set, the smelter re-opens the tap-hole at *a* to let out any still liquid slurry or lead, removes the slag from the channel leading to *b*, and makes some dams in the sand, of which its bottom consists. The smelter then thrusts a bar under the kettle-piece, whilst his

assistant drags it by a hook from the top of the pot. Should any lead be splashed during this operation into the channel, it is stopped by the dams just made. The lead in the pot is then skimmed, and the skimmings are laid aside with the "kettle-piece" for the next charge. A quantity of lead equal to what the smelter expects from the next charge is laded from the pot into moulds, and sent to the refinery. It contains from 500 to 800 ozs. of silver per ton. The smelters now rest till the charge is "warmed," and the fuel in the grate nearly burnt out. The clinker is then "broken," the grate "cleaned," and "fire" made. The damper is gradually opened as the fire burns up, according to the draught; so that the charge in the furnace may be ready to tap at its proper time (generally eight hours for 30 cwt.), but the smelters often "draw forward," so as to gain a charge or two per week. Although more work could be done by a strong draught and urging the fire, it is found better to keep within limits which ensure a clean slag: half an ounce of silver per charge is easily lost, and is enough to turn the scale against quicker work.

Whilst the damper is up and the charge in course of being melted down, the smelter and his assistant weigh out and wheel to the furnace the next charge, get in coals and scrap-iron, wheel out slurry, remove the slag from the pit *b*, and prepare for the next tapping.

When the charge is melted, the assistant draws a rake gently through the molten mixture to detach any scrap-iron adherent to the *tap-cavity*. If time will allow, the damper is lowered for 15 or 20 minutes to "let the iron work in the tap-cavity." When the iron is supposed to have done its work, the smelter drives a bar of iron about ½-inch diameter, through the clay in the *tap-hole*. The lead flows into the pot. If the charge yields more than is expected, a plug of dry clay is driven into the hole and some lead laded from the pot. The hole is re-opened: lead, followed it may be by slurry, runs into the pot and is allowed to flow through the notch at *a*. Lastly, slag begins to come from the furnace, when the notch at *a* is filled with a plug of wet clay. The smelter then drives a large bar of iron through the tap-hole, and on withdrawing it the slag pours into the pot and along the channel to the pit *b*. The working-doors of the furnace are opened, a rake passed over the bed, the sides fettled, etc., as before, and so the work goes on. About 15 cwt. of coal of inferior quality, just as it comes from the pit, are required to smelt a charge of 30 cwt. of silver-ore mixture. The slag contains about 1% of lead and less than 1 ounce of silver per ton. A furnace lasts many years, but requires a new arch every 12 or 18 months, with occasional repairs by the bricklayers and daily fettling by the smelters.

"SLURRY," *i.e.* REGULUS OR SPEISE, OR A MIXTURE OF BOTH.—The *slurry*—which consists sometimes of sulphides, sometimes of arsenides, but is generally a mixture of both—is treated in various ways. If it contains much lead, it is generally thrown back into the furnace, together with some scrap-iron. It is useful to work up in this way with mixtures which give no slurry. It assists the scrap-iron to melt

and act upon the slag besides its own action, which is advantageous in many ways, in the management of the *tap-cavity*.

Slurry nearly always contains copper, lead, and silver, sometimes nickel, cobalt, and other metals. It is roasted or calcined (both terms being here synonymous) in various ways, either in heaps on a bed of old timber with layers of charcoal, being "fired" thus two or three times; or it is calcined in any calciner of convenient shape. It is then melted with some suitable mixture to form a good slag. If very rich in silver and poor in lead, it may be requisite to add grey slag, but it generally contains enough of lead. Some scrap-iron is added, and the sand-pit at *a* is made larger. It is also generally divided, so that the smelter may separate the speise from the regulus. The latter is sold to the copper smelter. It generally retains 5 or 6 ozs. of silver per ton. Sometimes it is again calcined and remelted, being run from the furnace to the pit at *b*, fig. 83, the speise being turned to *a*. Or both may be run to *b* and the lead to *a*. When there is a large quantity to be worked containing only a very little lead, the pot in front of the furnace is generally emptied and filled with sand. The furnace is then worked like a copper-ore furnace, and the lead is stopped in a pit made in the sand-bottom, somewhere between the pot and the pit *b*, or it is run to *a*.

Speise.—The speise is generally calcined a second time, ground under edge-runners, mixed with culm or small cinders, and recalcined till nearly all the arsenic has been driven off. It is then melted with or without the addition of lead, and run from the furnace to *a* or *b* after proper additions to ensure a good slag. It is an interesting sight to see a smelter accustomed to such work divide the pit *b* into four divisions of various sizes, and tap the whole charge of 30 or 40 cwt. *over* the pot into the pit, getting nearly all the lead in one division, nearly all the regulus in another, nearly all the speise in another, and nearly all the slag in the last. When cold, the different substances are easily separated. The speise, containing generally 6 or 8 ozs. of silver per ton, is sold to the nickel and cobalt makers. [Page 525, line 21, *for* "1 or 2" *read* "3 hours," except for "sweep," when the former period suffices.]

PYRITIC SILVER-SMELTING.

By "Pyritic Silver-smelting" is meant the smelting of silver-ores, which are either free from lead or do not contain it in sufficient quantity to collect the silver, in conjunction with pyrites, in order to produce a regulus in which the silver may be concentrated; and the subsequent extraction of the silver from the regulus by means of lead. Iron-pyrites is used for this purpose, and by preference such as is argentiferous or auriferous; but, failing this sulphide, cupriferous iron-pyrites or copper-pyrites may be substituted. The choice of pyritic material must be determined by the possibility of procuring a supply of one or other of these minerals in the locality of the melting works.

Examples of Pyritic Silver-smelting, with the use of iron-pyrites,

are presented by the silver-lead smelting process at Sala, in Sweden, described in the Author's volume on the Metallurgy of Lead, pp. 296–303, and by the Kongsberg process, previously described in this volume, p. 507; and in the sequel a further account of this method of concentrating the silver in a regulus will be given in connection with certain *wet* methods of desilverizing such a regulus. A notice of Pyritic Silver-smelting is merely inserted in this place in order that the reader may be impressed with the fact of the existence of such a specific process, a description of which should naturally follow Silver-smelting in which lead is the vehicle throughout the process for collecting the silver.

Pyritic Silver-smelting is specially adapted to localities in which lead ores, or artificial products capable of yielding lead, are not procurable at a sufficiently low rate. Supposing the silver ores to be very poor, and to be incapable of economical concentration by dressing operations, as is generally the case, it is obvious that in smelting such ores in conjunction with lead ores, or products capable of yielding lead, there would be great loss of lead, owing to the necessary formation of a very large quantity of slag containing a notable amount of lead, to say nothing of the loss of lead by evaporation, which would also be considerable, especially if it be not practicable to avoid the formation of a slag which requires a very high temperature to render it sufficiently liquid to enable the regulus properly to separate and subside. But by means of pyrites it is possible in a single smelting operation to get rid of the great mass of foreign matter in the ore by converting it into slag, and thereby to obtain the silver in a concentrated state in the regulus. By partially roasting this regulus, which, let it be assumed, consists mainly of sulphide of iron, and smelting the product with the addition of a due proportion of silica, a second regulus, much richer in silver than the first, would be obtained. Or, the re-smelting of the partially roasted first regulus, in conjunction with siliceous silver-ore, would yield a second enriched regulus. By again repeating the smelting in the manner described, as was done in Lower Hungary,[1] a regulus still richer in silver might be procured; but experience has shown that the concentration of the silver in the regulus must not be carried too far, as in that case too much silver would be left in the slag. In the Kongsberg process it is not found expedient, on that account, to produce in the first smelting a regulus containing more than 80 ozs. of silver to the ton on the average, the extremes being 60 and 100 ozs. On this point, however, metallurgical writers do not appear to agree: thus, according to Wehrle, the silver should not exceed 41 ozs.[2] to the ton of regulus, and according to Kerl 65 ozs.[3]

With regard to the relation in weight between the regulus and the furnace-charge there seems to be nothing determinate. According

[1] Karsten, System der Metallurgie, 5. p. 536.

[2] Lehrbuch der Probier- und Hüttenkunde, 1844. 2. p. 403.

[3] Handbuch der metallurgischen Hüttenkunde, 1865. 4. p. 64.

to Wehrle, the best proportion of regulus at smelting works in Lower Hungary was found to be from 20 to 25 per cent. of the charge of ore,[4] whereas Kerl makes a general statement to the effect that it varies from 30 to 50 per cent.; but in this matter much must depend on the richness of the ore as well as the quality of the accompanying slag.

In the Altai mountains silver ores, containing much sulphate of baryta, are smelted in blast-furnaces by the Pyritic process, and, as a consequence, sulphide of barium is formed, which passes into the regulus to the extent of from 18 to 25 per cent., the remainder of the regulus consisting of sulphide of iron, copper, lead, zinc, and antimony. The regulus is desilverized by lead as at Kongsberg (see p. 510, B 3), so that the presence in it of so much sulphide of barium does not seem to interfere with this method of desilverization.[5]

DESILVERIZATION OF ARGENTIFEROUS REGULUS BY MEANS OF LEAD.

This process, it will be remembered, is in use at the Kongsberg Smelting Works, and a description of the mode of conducting it there is given at p. 510 antea. It is an ancient process, for, according to Schlüter, it was practised early in the 16th century at Kuttenberg in Bohemia, where the subject of treatment was an argentiferous copper-regulus produced in the following manner:—Argentiferous pyritic copper ores were smelted in the raw or unroasted state; the resulting regulus was roasted once and smelted in admixture with iron-pyrites and other argentiferous ores, by which means a second regulus was formed; and this regulus was smelted in the unroasted state with the addition of litharge (including hearth-bottom from the German cupellation furnace), argentiferous coppery lead, argentiferous leady copper, such as rich "Kiehnstock" (see p. 323 antea), "Frischschlacke" (see p. 311 antea), and slag resulting from this smelting. In the last operation an argentiferous alloy of copper and lead was formed, which, being suitable for liquation, was cast into liquation-cakes. The metal and regulus from the furnace were allowed to flow at intervals into a receiving pit of the usual kind previously charged with liquation lead poor in silver. The lead and regulus were well mixed by stirring, and, after the latter had risen to the surface and solidified, it was taken off in cakes, smelted repeatedly in conjunction with leady products, and finally converted into black-copper.[6]

In German metallurgical treatises this method of desilverizing with lead is described under the heading "Einränkarbeit," which literally means "soaking process;" and if the expression be restricted to this particular manipulation, it seems to be not inappropriate. But according to some German authors, Wehrle for example, it has a much wider signification, and extends to the entire process of

[4] Op. cit. 2. p. 404.
[5] Berg- u. Hüttenmännische Zeitung, 1853. 12. p. 137.
[6] Gründlicher Unterricht von Hütte-Werken, 1738. p. 473.

Pyritic Silver-smelting, of which the "soaking process" is only one stage. The expression "Lead-soaking process," I venture to suggest, might be conveniently adopted in English. As the lead-soaking process was not always conducted in exactly the same manner, it may be well to mention in this place the modifications of it of which an account has been published: they are as follow:—

I. Mixing molten lead with the molten regulus in the fore-hearth of a blast-furnace, *i.e.* that part of the hearth which projects beyond the tymp and is open at the top, and over which a jet of flame is allowed to escape from the breast of the furnace, in order to keep the contents of the fore-hearth in a molten state.

II. Mixing molten lead with the molten regulus after the latter has been tapped into a cavity separate from the furnace.

III. Hydrostatic method, so called, in which the intermixture of the molten lead and regulus is effected, by causing the former to *ascend*, by small portions at a time, through the latter, with a view of effecting better intermixture.

The regulus should in all cases be as thinly liquid as possible.

DETAILS CONCERNING THE INTERMIXTURE OF LEAD AND REGULUS.

No. I. In the district of Nagybánya, in Hungary, the process is conducted in the following manner.[7] For 12 ctr. of regulus, produced in smelting 100 ctr. of argentiferous pyritic ore containing gold, from 4 to 6 ctr. or more of lead are used, in direct proportion to the richness of the ore in silver. The lead is divided into as many portions as the number of tappings; and before each tapping one of these portions of lead is put into the fore-hearth. The regulus and lead are tapped off together into a circular brasqued pit adjacent to the furnace. The regulus, as it solidifies, is taken off in discs. When the lead is found to contain at least 20 loths of silver per ctr., it is cupelled; but if not, it is used over again. It is stated that from $\frac{1}{3}$ to $\frac{1}{2}$ of the silver, and from $\frac{1}{2}$ to $\frac{2}{3}$ of the gold, are thus extracted from the regulus and concentrated in the lead. The desilverized regulus retains from 2 to 6 loths of silver per ctr.; but the proportions of silver and gold vary in the different discs inversely as the time of contact between the regulus and the lead, so that discs first removed contain more silver and gold than the others, between which and the lead contact has been more prolonged.[8]

No. II. This is the method practised at Kongsberg, and the only difference, if difference it can be called, between it and that of No. I. is that in the latter the intermixture of the lead and regulus takes place in the smelting furnace, whilst in the former it takes place outside the furnace in a pit into which the regulus has been tapped.

The following description of the process, as practised in Hungary,

[7] In the following descriptions the present tense is used, although the processes may have been abandoned.

[8] Karsten, System der Metallurgie, 5. p. 559.

is given by Wehrle.[1] The quantity of lead used is proportionate to that of the silver in the regulus, and varies in weight from 42% to 55% of the regulus, which contains from 25 to 33 loths of silver per ctr. From 425 to 550 lbs. of lead are required for each tapping of regulus, according to its richness in silver. The tapping-pit is well heated by means of incandescent charcoal and the lead melted therein, after which the regulus is run into it and well mixed with the molten lead by stirring with an iron hook, or, as Gruner states, with a rod of iron twisted spirally at the end.[2] After stirring, as soon as a thin crust of regulus has formed on the top, it is taken off with a fork. What remains in the tapping-pit is stirred again, and a second thin disc of regulus is taken off, and so on until the whole is removed, a thin layer of regulus being always left on the bath of lead in order to prevent oxidation or mechanical loss of lead.[3] About 20 minutes after the completion of this operation, the furnace is again tapped, and the same manipulation as above described is repeated. The whole process lasts about 8 hours with the same dose of lead, which, after this period, will be sufficiently rich in silver for cupellation, when it is, consequently, replaced by fresh lead for the next operations. As the regulus, after the foregoing treatment, still retains from 14 to 20 loths of silver per ctr., it is roasted and added to the charge in ore-smelting.

At Kolywan, in the Altai mountains, in pyritic silver-smelting desilverization is effected in a separate hearth provided with a blast and common to two smelting furnaces. After the hearth has received its charge of molten regulus, charcoal is laid over the top and the lead placed thereon, so that, as it melts, it trickles down through the charcoal and the regulus, thus coming largely in contact with the latter. From 5% to 10% of pig-iron, either granulated or in fragments, is put into the molten regulus, in order that, by liberating lead and silver therefrom, desilverization may be promoted. The lead is added in 4 equal portions, by weight, successively, about 25% of the weight of the regulus each time; and after each addition the molten mass is poled with sticks of green wood, and the lead is tapped off. The first portion tapped off generally contains about 170 ozs. of silver per ton, and is cupelled; and the second portion tapped off is used in the first stage of desilverizing the next batch of regulus, and so on.

The regulus contains about 64 ozs. of silver per ton, and 36 cwt. of it constitute one charge in the hearth. After desilverization it retains from $8\frac{1}{2}$ to 17 ozs. of silver per ton.

Formerly the regulus to be desilverized was re-melted in a much larger hearth, and not run in direct from the furnace; a process obviously less economical than that above described.[4]

No. III. In this method, the argentiferous regulus, as it leaves the

[1] Lehrbuch der Probier- u. Hüttenkunde, 1844. 2. p. 413.

[2] Notice sur le traitement des minerais auro-argentifères dans la Basse-Hongrie. Ann. des Mines, 1836. 3rd series, 9. p. 42.

[3] Gruner, op. cit.

[4] Berg- u. Hüttenmännische Zeitung, 1853. 12. p. 160.

furnace, is made to flow upwards through a column of molten lead, in the manner presently to be described. Smelting is effected in a low blast-furnace (*Krummofen*), having a round, comparatively deep fore-hearth, nearly wholly outside the breast. This fore-hearth is divided into two chambers by a partition wall of refractory material, reaching nearly to the bottom, and parallel to the fore-wall. The bottom of the partition wall rests on a plate of iron set horizontally, and extending some distance beyond the front of that wall. The fore-hearth and the side of the partition wall facing the furnace are coated with a brasque of clay and charcoal in the usual manner. Molten lead is let into the fore-hearth until it has risen somewhat above the bottom plate of iron. The slag and regulus run direct from the furnace into that part of the hearth which is contiguous to the breast and which is open at the top, slag overflowing as the regulus accumulates underneath. After a time the height of the molten regulus on the inner or furnace side of the partition wall becomes sufficient to enable it to escape through, and rise to the top of, the molten lead on the outer side of that wall. The object of the extension forwards of the bottom plate of iron is to prevent the regulus from ascending by the side of the partition wall, and to cause it to rise through the central portion of the mass of molten lead, whereby contact between it and the lead may be increased. A furnace of the kind above described is represented in the engravings in the Atlas to Karsten's System of Metallurgy, Nos. 979 to 981. The process was tried at Siegen and abandoned. The quantity of slag produced in the first smelting proved to be so large as seriously to interfere with the process, and it was found better to operate upon the regulus re-melted by itself. But even after a repetition of this operation, not more than $\frac{4}{7}$ths of the silver were extracted.[5]

The chief advantages of the process of desilverizing argentiferous regulus by the "lead-soaking process" are as follow:—

I. The extraction of a large part of the silver from the regulus while it remains molten, either in the hearth of the furnace, or immediately after it is tapped off, and obtaining an alloy of silver and lead suitable for direct cupellation; and it need hardly be remarked that, in the case of a precious metal like silver, it is very important, in a financial point of view, to render it marketable as soon as possible.

II. The possibility of carrying on silver-smelting in localities where lead is scarce and comparatively dear, and where it might not be desirable to incur the expense of erecting a plant for the desilverization of the regulus by *wet* methods.

Argentiferous regulus is more completely desilverized by smelting it with the addition of lead-ores or lead-yielding substances; but, on the other hand, the loss of lead, and of copper also in the case of cupriferous regulus, is considerably greater than when the "lead-soaking process" is adopted.

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[5] Karsten, System der Metallurgie, 5. p. 520.

It is asserted by Gruner, and by Rivot and Duchanoy (see footnote [3], p. 540), that when gold is present in the regulus, it is extracted in relatively larger proportion than silver by the "lead-soaking process."

By a single desilverization with lead at Kongsberg the silver present in a regulus to the amount of about 1·5% was reduced to from 0·75% to 1% (*i.e.* a reduction of 50% and 33% respectively); and in Lower Hungary the reduction varies from 20% to 60%.[6] At the Altai Works, by four successive desilverizations, the reduction was from 75% to 80%.

DESILVERIZATION OF ARGENTIFEROUS COPPER-REGULUS BY MEANS OF LEAD AND COPPER CONJOINTLY.

(*Abdarrarbeit* and *Kupferauflösungschmelzen*, of the Germans.)

Drying-off Process (*Abdarrarbeit*).

Suppose argentiferous pyritic copper-ore, say, a mixture of yellow and grey copper ore or "Fahlerz" (*i.e.* arsenio- or antimonio-sulphide), to be smelted and an argentiferous regulus produced containing about 30% of copper, the treatment of this regulus is as follows:—The regulus (A) is roasted but not "sweet," and smelted with the addition of lead-ore, substances containing oxide of lead, and argentiferous alloys of copper and lead in varying proportions; and the products are regulus (B) containing about 35% of copper, 45% of lead, and 3½ loths of silver per centner,[7] and an alloy consisting of about 20% of copper, 80% of lead, and 10 l. of silver per ctr., which alloy is cast into liquation-cakes. The regulus (B) is smelted unroasted with various argentiferous alloys of copper and lead, and the products are what is termed "twice-leaded regulus" (C), containing about 45% of copper, 25% of lead, and 3 l. of silver per ctr., and an alloy consisting of about 20% of copper, 80% of lead, and 6 l. of silver per ctr., which alloy is also cast into liquation-cakes and liquated. The regulus (C) is smelted unroasted with an alloy consisting of about 60% of copper, 30% of lead, and 4½ l. of silver per ctr.; and the products are a regulus (D), named "once-dried regulus," which contains about 50% of copper, 25% of lead, and 2½ l. of silver per ctr., and an alloy consisting of about 30% of copper, 70% of lead, and 5½ l. of silver per ctr. This operation is termed "Abdarren" by the Germans, and literally means "the drying off." The regulus (D) is smelted unroasted with alloys consisting of about 70% of copper, 25% of lead, and 2 l. of silver per ctr.; and the products are regulus (E), named "hard or twice-dried regulus," which contains about 55% of copper, 15% of lead, and 2 l. of silver per ctr., and an alloy consisting of about 60% of copper, 30% of lead, and 4½ l. of silver per ctr. At some works the "Abdarren"

[6] Wehrle, op. cit. 2. p. 414.

[7] In this case 1 loth = 0·03125% = 10 ozs. 4 dwt. 4 grs. per statute ton of 2240 lbs. avoirdupois. The centner usually consists of 100 lbs. 1 lb. = 2 marks = 32 loths. In the following descriptions ctr. will be used as the abbreviation for centner, and l. for that of loth.

is repeated a third time. The regulus (E) is roasted several times and smelted with the addition of siliceous copper-ores and acid copper-slags; and the products are copper-regulus (F), containing about 65% of copper, and from ¾ to 1 l. of silver per ctr., and an alloy containing about 70% of copper, 25% of lead, and 2 l. of silver per ctr.: this alloy is treated along with the regulus (D), as above described. The regulus (F) is roasted and smelted for black-copper, etc. As the slags resulting from the preceding operations contain too much metal of value to be thrown away, they are subjected to further treatment involving the following operations, namely, lead slag-smelting, lead slag-regulus smelting, regulus slag-smelting, "roast" slag-smelting, and copper slag-smelting. The various furnace residues and flue-dust are treated along with the slag. The silver and lead are collected in the various intermediate products, and the copper finally in a rich regulus, from which marketable copper is obtained. The intermediate products all go back for treatment in the operations just described.

The foregoing process, which is the "Abdarrarbeit" of the Germans, may be regarded as consisting of two stages,—the first, in which the iron of the original regulus being oxidized and slagged off is replaced by copper and lead; and the second in which the lead is simply replaced by copper, a copper-regulus being obtained in the last instance as free from silver and lead as is economically practicable. In both stages the alloy of copper and lead is used in excess.

It may be asked, Why the expression "Abdarren" or "drying off" should be applied to this process? An answer may probably be suggested by the following considerations. The treatment of the coppery residues, resulting from the liquation of argentiferous copper in the old process of liquation, is termed "Darren," which, literally translated, means "drying." Now, in this treatment, the residues are deprived of a large part of the lead which they have retained, and being thus freed from lead, which melts at a very low temperature in comparison with copper, may be said to be "dried," as it were. In the "Abdarrarbeit," the regulus becomes also freed from lead, and may also be said to be "dried." It is true that in the liquation process the German word is "Darren," and not "Abdarren;" and there is the same difference between the meaning of these words as between the English words "drying" and "drying off;" but what the difference is it must be left to the reader to determine.

This process was in operation at Brixlegg in the Tyrol at the end of the last century, and, according to Kerl, continued to be practised there in 1865. A description of it was published by Von Born in 1789;[8] and it has also been described by Karsten, Wehrle, and Kerl. The preceding account of it is extracted from that of Kerl, who states that his information on the subject was partly derived from a private source.[9] Von Born expresses a favourable opinion of this process in comparison with others, notwithstanding its complexity

[8] Bergbaukunde, 1789. 1. pp. 217–237. [9] Handbuch, 1865. 4. pp. 96 et seq.

he length of time which it required. Karsten ascribes to this
ss the following advantages:—Very satisfactory (*sehr voll-
ige*) extraction of the silver, small loss of copper, and the pro-
on of copper of particularly good quality. He further remarks
it is only applicable to the treatment of such silver ores as
in sufficient copper for the collection of the silver.[1]

COPPER-DISSOLVING-SMELTING (*Kupferauflösungschmelzen*).

n the "Kupferauflösungschmelzen," which means literally
per-dissolving-smelting," the silver is extracted from an argen-
ous copper- and lead-regulus, and argentiferous black-copper,
ced in the smelting of silver-ores containing lead in admixture
other silver-ores. The process consists of the following opera-
:—Supposing the regulus to contain not less than 18% and not
than 30% of copper, from 10% to 20% of lead, and from 2 to 4 l.
lver per ctr., it is roasted twice and smelted in a low blast-
ce with the addition of 80% of poor (*i.e.* in silver) or coppery
rge, and from 10% to 12% of black-copper containing less than
of silver per ctr., 5% of metallic iron and 50% of slag; or if more
ch black-copper is available, its proportion may be increased up
%, but in that case the regulus is not roasted. The furnace-
ge should, on the average, contain from 30 to 40 lbs. of copper
to 5 l. of silver per ctr., and for every loth of silver from 15 to
s. of lead. Instead of litharge roasted lead ores may be used.
products are lead amounting to from 80% to 90% of that existing
e charge, and containing from 3 to 5 l. of silver per ctr.; regulus
aining from 36% to 50% of copper, 12% to 20% of lead, from 2 to
of silver per ctr.; and slag containing from 2% to 3% of lead by
ssay and 15% by *wet* assay (!), from $\frac{1}{4}$% to $\frac{1}{2}$% of copper by *wet* assay,
denär of silver per ctr. (1 oz. 5½ dwt. per ton). The regulus
be desilverized by smelting it (always in a blast-furnace) in
aw state with the addition of 5% of iron, and adding lead to the
n regulus in the hearth; or by roasting and smelting it with
rge. For every loth of silver in the furnace-charge, inclusive
e lead put into the hearth, there should be present from 20 to
s. of lead, because, with a smaller proportion, the regulus would
n too much silver, yet not sufficient to bear the cost of a repeti-
of the process. The products are poor lead, which amounts to
80% to 90% of that in the charge, and contains from 3 to 5 l. of
per ctr.; desilverized copper-regulus containing from 50% to
of copper, from 10% to 15% of lead, and from 3 quints to 1 l.
lver per ctr. (7½ to 10 ozs. per ton); and slag. The amount
gulus produced varies from 50% to 80% of the furnace-charge,
ding as the original regulus was or was not roasted. The
us is repeatedly roasted and then smelted for black-copper,
n, after having been refined, contains from 1½ to 2½ l. of silver
tr. (15 to 25½ ozs. per ton).

[1] System der Metallurgie, 5. p. 520.

The slag is richer in lead when litharge forms part of the smelting charge; but the greater loss of lead from this cause is compensated for by an increase in the yield of silver.

The process was conducted as above described in the Nagybánya district in Upper Hungary in 1832, and the description has been abstracted from that published by Wehrle.[2] It should be stated that it is only the presence of gold in the poor Hungarian silver-ores that renders their treatment profitable by this process.

By comparing the foregoing descriptions of the "Abdarr" and "Kupferauslösung" processes, it will be seen that in the former the argentiferous regulus is smelted repeatedly with an excess of alloys of copper and lead; while in the latter, the regulus is smelted with only as much black-copper as it is capable of dissolving, or, what is equivalent in meaning, of converting into sulphide. Besides, in the "Abdarr" process the silver is concentrated in an alloy of copper and lead suitable for liquation; while in the "Kupferauslösung" process nearly the whole of the copper of the argentiferous copper treated passes into a regulus desilverized as far as is economically practicable, and the silver is concentrated in the lead, which, however, by repeated use becomes so coppery as to require to be liquated before cupellation. Liquation in this case means simply heating the alloy at a low temperature on the bed of any suitable furnace, when the lead flows away, leaving the copper in an unmelted state; it is, in fact, the reverse of the process described at p. 343, in which the copper is separated during the slow cooling of an alloy of lead and copper.[3] The liquated lead is cupelled when it contains 8 l. of silver per ctr., *i.e.* about 82 ozs. per ton.

DESILVERIZATION OF ARGENTIFEROUS SPEISE BY LEAD.

In the process of smelting at Freiberg there is produced a speise containing about 40% of copper, 10% of lead, 2·5% of nickel and cobalt, and from 0·4% to 0·5% of silver (about 163 ozs. per ton), the remainder consisting chiefly of iron and arsenic. In recent times, instead of repeatedly smelting the roasted speise with leady products,[4] it is simply smelted in a small reverberatory furnace, with the addition of a mixture of from 20% to 25% of quartz and from 50% to 60% of sulphate of baryta, after which the resulting slag is drawn off and metallic lead put into the furnace in the proportion of $1\frac{1}{2}$ part by weight for 1 part of speise, when the whole is thoroughly rabbled and the lead tapped off. The products are lead which contains 0·2% of silver, copper-regulus, and speise rich in nickel, containing 0·02% of silver (about $6\frac{1}{2}$ ozs. per ton).[5]

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[2] Lehrbuch der Probier- u. Hüttenkunde, 1844. 2. pp. 425 et seq. See also Karsten's System der Metallurgie, 5. p. 556; and Kerl's Handbuch, 1865. 4. p. 95.

[3] Voyage en Hongrie exécuté en 1851 par MM. Rivot et Duchanoy, ingénieurs des Mines. Annales des Mines, 1853. 5th series, 3. p. 270.

[4] For details respecting this treatment of the speise, see the Author's volume on the Metallurgy of Lead, p. 318.

[5] In the original the words are "Man

The sulphate of baryta in the smelting operation above mentioned has an oxidizing action, owing to the oxygen of its sulphuric acid, which acid would be displaced by the silica, with the formation of silicate of baryta; and so this treatment would in effect be equivalent to roasting. If any mixture consisting of nickel, iron, arsenic, oxygen, and silica, be strongly heated, arsenide of nickel and ferrous silicate will be formed, provided as much arsenic is present in the state of arsenide as suffices to combine with the nickel and produce speise.

In the Lower Harz a "very coppery, leady speise," containing about 1·6% of cobalt and 0·7% of nickel, is treated in a Germam cupellation furnace in the same manner as impure argentiferous lead. The products are "Abzug" (*i.e.* the substance which rises to the top during fusion), which melts with difficulty, slag, and argentiferous "black-copper," which latter is desilverized. The "Abzug" is smelted for copper-regulus and speise, and the slag for antimonial lead and speise: the speises thus produced contain from 3% to 6% of cobalt and, at the highest, 0·8% of nickel; but it is not stated how much silver existed in the original speise, or how much remained in the resulting speises.[6]

SILVER-SMELTING IN THE PILZ BLAST-FURNACE AT FREIBERG.

Although a full description of the process of smelting at Freiberg appeared in the Author's volume on the Metallurgy of Lead, published in 1870, yet as the process since that time has been much altered, owing to the introduction of a particular blast-furnace which appears to be well adapted to the smelting of silver ores generally, a short description of the method of smelting as now practised at Freiberg will be here presented. This furnace is the invention of Mr. Pilz, formerly manager of the Halsbrücke Smelting Works, and at present Assistant General Manager of the government smelting department at Freiberg; and it was first introduced at those works in 1866. For the following information on the subject I am indebted to Mr. Godfrey.

Since the end of 1863 the blast-furnaces, like that described in the Author's volume on the Metallurgy of Lead (pp. 309 et seq.), and known as Wellner's double furnace, have been gradually changed into blast-furnaces which have closed breasts and water-twyers, and are charged in the same manner as an iron smelting blast-furnace; that is, the ore-mixture and fuel are spread in horizontal layers, instead of the former being thrown in towards the back-wall and the

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erhielt Werkblei von 20 Pfdth. Silber im Ctr. Kupferstein und hochhaltige Speise mit 2 Pfdth. Silber im Ctr." (Vorlesungen über Allgemeine Hüttenkunde von Carl Friedrich Plattner, 1860. 2. p. 353.) It is not clear whether the content of silver in the last line refers equally to the regulus and speise. If it refer to the latter only, the distribution of the original silver may be accounted for, the quantity in the regulus not being stated; but if it refer to both, there is an unexplained loss of silver.

[6] Kerl. Die Rammelsberger Hüttenprozesse, 2nd ed. 1861. p. 53.

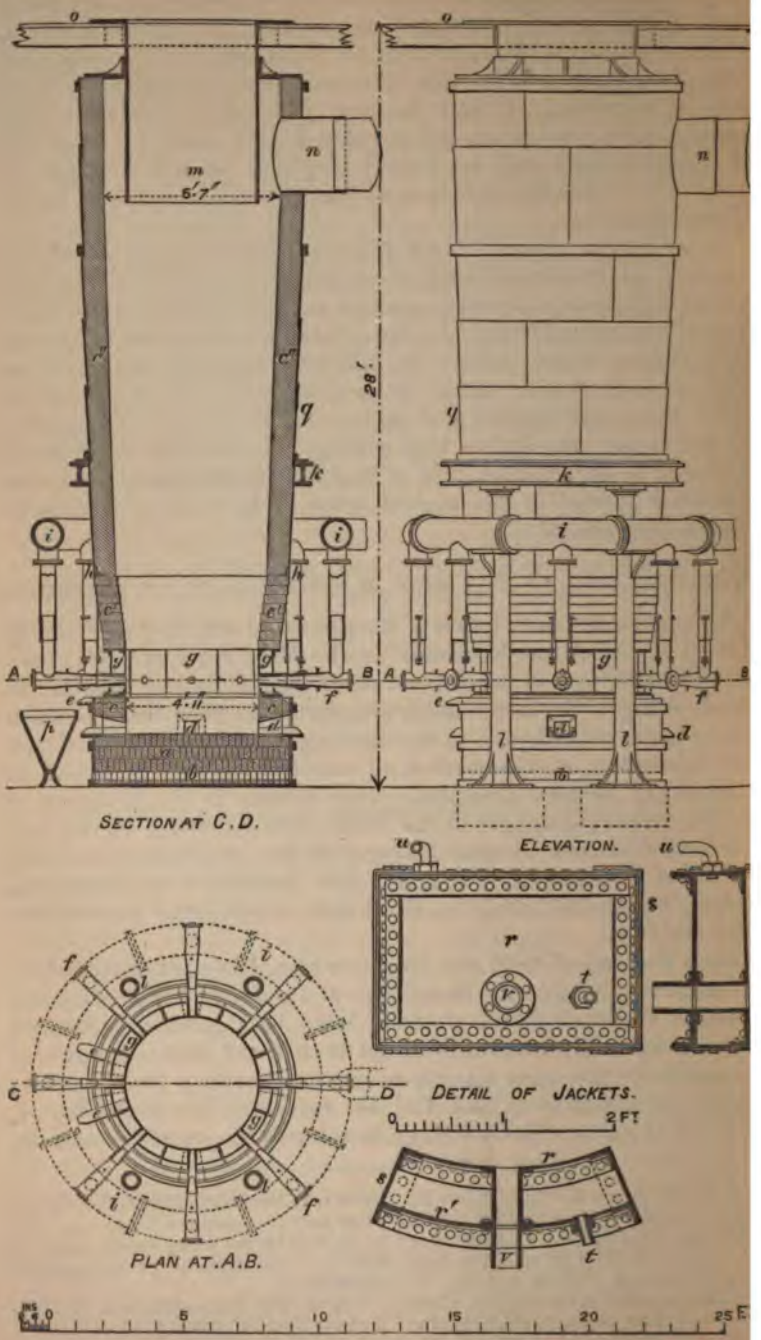
SECTION AT C.D.
ELEVATION.
DETAIL OF JACKETS.
PLAN AT A.B.
28'
5'7"
4'11"
2 FT
0
5
10
15
20
25 FEET

Fig. 84.

ıtter towards the front-wall. In the accompanying engravings of ıe Pilz furnace all the most recent improvements up to May 1878 re represented.

Quite recently a wrought-iron trough running on wheels has been ıbstituted for the tapping pit, and found to answer very well. The rough when full is taken to a cool part of the furnace-house, where he separation and removal of its various contents are effected. A rough of cast-iron was first tried, but found not to answer on account f its liability to crack.

PRESENT PROCESS OF SMELTING AT FREIBERG.

Formerly pyritic ores poor in silver and free from lead were melted together with slags from the smelting of lead-ores in reverberatory furnaces (*Roharbeit*); and the resulting regulus (*Rohstein*), after having been roasted, was used as a flux in ore-smelting in blast-furnaces (*Bleiarbeit*). But the "Roharbeit" has been given up, and at present all ores, excepting copper-ores and cupriferous products containing little silver and no lead, are mixed together, roasted, and smelted in the Pilz furnace. The roasting is so conducted as to cause the ore to agglomerate or sinter together into more or less melted lumps, in which state it is put into the blast-furnace; whereas, until recently, the ore was for the most part in a powdery state when charged. Moreover, in the former process the lead-regulus (*Bleistein*) from ore-smelting, previously to its concentration in reverberatory furnaces, had to be subjected to a separate smelting,

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Fig. 84. Description of Pilz's furnace (p. 542).

a. Hearth-bottom: it consists of four courses of bricks, the lowest one of common red brick and the others of fire-brick; the brickwork rests on a circular plate of cast-iron 1½″ thick, and is encased with boiler-plate, in four segments screwed together at the sides, which are flanged for that purpose, the casing being further strengthened externally by three strong hoops of wrought-iron.

b. Channel extending through the brickwork and open at each end; it is intersected at right angles in the centre by another similar channel, of which the section is shown at *b*: the object of these channels is to promote the escape of moisture.

c, *c*. Courses of fire-brick forming the inner and upper part of the hearth.

c', *c'*. Courses of fire-brick at the boshes.

c'', *c''*. Courses of fire-brick forming the shaft.

d, *d*. Tap-holes: each furnace has four tap-holes, the positions of which are indicated in the plan by dotted lines, and by full lines in the vertical section on the line C D of the plan.

e, *e*. Two cast-iron gutters for the outflow of the slag.

f, *f*, etc. Blast-pipes, the horizontal portions of which can be moved to and fro in the twyer-holes by means of two small handles, the positions of which are indicated by short lines in the elevation and section, and by small circles in the plan; and there is also a sliding-screw arrangement by which the vertical portions of those pipes may be moved up and down, as shown in the elevation.

g, *g*, *g*. Water-jackets of wrought-iron, of which the construction is shown in detail in separate figures under the elevation.

h h. Ring of angle-iron, rivetted to the outer casing, and intended for the support of the shaft during the reparation of the lower part of the furnace.

i i. Blast-main of cast-iron.

k. Ring of double-T iron supported by cast-iron pillars.

l, *l*, etc. Four pillars of cast-iron for supporting the ring *k*.

m. Cast-iron cylinder, flanged at the top, inserted in the mouth of the furnace in order that the waste-gas and fume may be drawn off.

n. Pipe for drawing off and conveying the waste-gas and fume to the condensing chambers, exhaustion being effected by a chimney communicating with the latter.

o. Charging-floor.

p. Slag-pot or conical vessel of cast-iron into which the slag flows.

q. Outer casing of sheet-iron.

r, *r'*. Inner and outer wrought-iron plates, ¼″ thick, forming the water-jackets at the upper part of the hearth: they are rivetted to angle-iron 2¾″ × ¾″.

s, *s*. Slide-plates overlapping by 2¾″ at the top and bottom.

t. Pipe for supplying cold water.

u. Pipe for the outflow of the heated water.

v. Twyer, 2¾″ in diameter.

which has been suppressed, the roasted regulus being now smelted in the Pilz furnace in conjunction with the ore-slag, in order to render the latter sufficiently clean to be thrown away. Formerly from 3% to 6% limestone was added to the charge in ore-, regulus-, and slag-smelting; but it has been found that this addition is unnecessary, and that these smelting operations may be carried on as well without it.

Ore-smelting.

Composition of the Charge.—The various ores delivered at the Freiberg Smelting Works, of which a detailed description is given in the Author's volume on the Metallurgy of Lead, are mixed in the following proportions:—

	Per cent
Lead ores, containing above 30% and up to 70% of lead	27-36
Do. do. above 15% and up to 30% do.	6-18
Pyritic ores, do. above 25% or more of sulphur	39-48
Do. quartzose, do. from 10% and up to 25% do.	4-16
Do. do. do. under 10% do.	3 12
The ore mixture contains of lead	18·28
Do. do. of zinc	8-17
Do. do. of copper	1-5
Do. do. of silver	0·08-0·60
Do. do. of sulphur	3 5-5

Foreign argentiferous copper-ores are now smelted in admixture with ores raised from the Freiberg mines; and from the former the copper in the products is mainly derived; jewellers' and silversmiths' "scrap" and "sweep" are also added to the charge in ore-smelting. The pyritic ores are passed through a Gerstenhöfer roasting furnace, and then mixed with lead-ores, after which the mixture is roasted in long reverberatory furnaces, named "Fortschaufelungsöfen," whereby it becomes sintered, and more or less melted, together. The roasted ore is smelted with the addition of from 90% to 100% of the slag produced in this operation, of various substances impregnated with metal, such as the material removed in rebuilding or repairing the furnaces, and of plumbiferous residues rich in silver resulting from the processes of liquation, cupellation, and the refining of "Blicksilber."[†] The proportions of the ingredients of the smelting charge should be so regulated as to yield a slag containing not less than from 27% to 30% of silica, or even a somewhat higher percentage if practicable.

Fuel.—The fuel is coke from Waldenburg, in Silesia, which yields from 8% to 12% of ash, whereas formerly coke from Potschappel near Dresden and from Zwickau was used, the former yielding from 18% to 25% of ash; and the latter, from 12% to 16%.

Mode of charging and working the Furnace.—Smelting is always conducted with a "dark top" (*i.e.* without flame at the mouth), and either without a "nose" (*i.e.* slag prolongation of the twyer) or with only a very short one. The coke is thrown into the middle of the furnace, except when the noses have become too long, in which case

[†] See the Author's volume on the Metallurgy of Lead, p. 210.

thrown in towards the circumference, a few charges of coke so ibuted generally sufficing to reduce the noses to the desired :h. When there are no noses, a larger supply of water will be sary to keep the jackets, which it will be borne in mind form pper part of the hearth, sufficiently cool. Nozzles for the blast- varying in diameter from $1\frac{3}{8}$″ to $1\frac{5}{8}$″ are used according to mstances. The blast is cold, and generally its pressure ranges $\frac{3}{4}$″ to 1″ of a column of mercury, but in exceptional cases it creased to $1\frac{3}{8}$″ and $1\frac{5}{8}$″. The quantity of air injected into a ace varies from 800 to 960 cubic feet per minute, and sometimes nts even to 1410 cubic feet.

QUANTITY SMELTED DAILY.—On the average from 550 to 700 ers of ore are now smelted in 24 hours (1878); and formerly, n there was a large quantity of ore in stock, as much as 1000 and 1200 centners were smelted in the same time. In the latter however, the pressure of the blast had to be increased; and gh the slags were not so clean as at present, yet there was really reat disadvantage in this, because all the slags which were pro- d had to be re-smelted.

CONSUMPTION OF FUEL.—The coke consumed is 1 centner to from 7 centners of the ore, or to from 10 to 13 centners of the smelting ure, which is equivalent to from 14% to 20% of the ore.

LABOUR.—For a furnace of the size shown in fig. 84 five men are antly required; namely, one smelter, two chargers, and two tants. They are paid on the piece-work system; that is, accord- to the quantity smelted. The smelter earns from 2·7 to 3·3 s (1 mark = $11\frac{3}{4}d.$) per shift of 12 hours, and each of the other from 2·3 to 2·8 marks. This work includes, in addition to the ging and management of the furnace, the removal and emptying e slag-pots on the ground, where the slag before being re-smelted oken up by another set of men.

PRODUCTS AND YIELD.—The products are as follow:—Lead, con- ng a very variable proportion of silver; regulus, which amounts om 6% to 9% of the weight of the ore smelted, and contains from to 40% of lead, from 6% to 17% of copper, and from 0·08% to of silver; and slag, which contains from 2·5% to 4·5% of lead, from 0·005% to 0·04% of silver (1 oz. 12 dwts. 16 grs. to 13 ozs. t. 8 grs. per ton).

he lead contains from 0·5% to 0·7% of copper, and is therefore cted to liquation, which is effected by cautiously heating it e sloping bed of a furnace so as to leave an unfused residue ining most of the copper. By this treatment the copper in iquated lead is reduced to 0·2% or 0·3%. The lead after being ed is subjected to the Pattinson process, when most of the r which it retained passes into the skimmings, the resulting etable lead not retaining more than 0·03% or 0·04% of copper.

peise is only occasionally produced: it consists chiefly of arsenide pper and contains from 20% to 25% of copper, from 0% to 2% of l and cobalt, and from 0·1% to 0·2% of silver.

The slag is variable in composition, and contains from 26% to 32% of silica, from 1% to 2·5% of lime, from 39% to 42% of protoxide of iron, from 8% to 16% of oxide of zinc, from 0·25% to 0·4% of cuprous oxide, and from 0·5% to 1·5% of sulphur.

In former times, when the ores were smelted with the addition of from 150% to 200% of slag from the same operation, and, consequently, when the quantity of ore daily smelted amounted only to from 300 to 400 centners, slags were produced which contained from 2% to 2·1% of lead, and from 0·0015% to 0·0025% of silver, which were thrown away. But subsequently it has been found more economical to smelt a larger quantity of ore with a less quantity of slag, and subject the resulting slags to a separate smelting as above stated. Twice-smelted slags are of course freer from mechanically entangled metalliferous matter than such as are only once smelted, so that in twice smelting there is less reason to depend upon the care of the workmen for obtaining clean slags.

Blende.—In the smelting of ores rich in blende, such as are treated at Freiberg, great attention is required in the roasting of the ores. When the roasting has been imperfectly conducted, not only are the resulting slags richer in lead, and consequently also in silver, but there is great difficulty in rendering them clean enough by re-smelting; and, moreover, the accompanying regulus is richer in zinc and lead, and the separation of it from the slag is very imperfect, making it difficult to perceive the line of demarcation between the two. Such mixtures of slag and regulus, even when re-melted, will hardly produce a sufficiently clean slag, if they have not been previously roasted.

Silica.—By the use of Pilz furnaces, with a hearth somewhat more contracted than is shown in fig. 84, excellent results have been obtained in the smelting of very silicious ores, and clean slags containing from 39% to 43% of silica have been produced in the smelting of the ores of Mansfeld or of the Upper Harz.

Regulus and Slag-smelting.

Furnace Charge.—The regulus is broken into lumps and roasted twice: the first time in closed kilns, such as are used for burning iron-pyrites in the manufacture of sulphuric acid, by which treatment the sulphur is reduced to 6% or 8%; and the second time in what are termed "Wellner's roasting stalls," which consist of a long truncated rectangular pyramidal bed surrounded by low walls, with fireplaces at the lower part of each end wall. Slags from ore-smelting, of the composition previously stated, are smelted in the same kind of furnace as that used in ore-smelting, with the addition of from 6% to 9% of roasted regulus, besides various leady products poor in silver, such as cupellation hearth-bottoms, litharge, skimmings from Pattinson's process, and, if available, the material, poor in silver, which is removed in the rebuilding or repairing of furnaces.

Details respecting the Blast.—The nozzles of the blast-pipes vary in diameter from $1\frac{3}{16}$″ to $1\frac{3}{8}$″, and generally the pressure of the blast ranges from $\frac{3}{8}$″ to $\frac{5}{8}$″ of a column of mercury; but when necessary it

is increased up to 1". The quantity of air injected into the furnace varies from 640 to 880 cubic feet per minute, and sometimes amounts to 1240 cubic feet.

Mode of charging.—The charging is effected in precisely the same manner as in ore-smelting.

Quantity smelted daily and Fuel consumed.—In 24 hours from 800 to 900 centners of slag, exclusive of regulus and other materials of the charge, are smelted, with a consumption of 1 centner of Silesian coke to from 9 to 12 centners of the total charge.

Products and Yield.—The products are as follow:—Coppery regulus, containing from 22% to 26% of copper, from 8% to 12% of lead, and from 0·08% to 0·16% of silver; lead, containing from 0·2% to 0·6% of silver; and slag, which contains from 1·5% to 2% of lead and from 0·001% to 0·0015% (6 dwts. 13 grains to 9 dwts. 19 grains per ton) of silver, and which is thrown away, except such as retain shots of regulus, which is re-smelted in subsequent regulus and slag-smelting.

Treatment of Coppery Regulus.—The regulus is twice roasted in the same manner as the first regulus, and then smelted in reverberatory furnaces in order further to concentrate the copper. All copper ores and coppery products poor in lead and silver are added to the charge; and the subsequent treatment of the resulting copper regulus remains substantially the same as stated in the Author's volume on the Metallurgy of Lead (pp. 333 et seq.), namely, dissolving out the oxide of copper in the copper regulus, roasted sweet, by boiling dilute sulphuric acid.

Superiority in Economical Results of the Pilz Furnace to that formerly used at Freiberg and known as the Wellner Furnace.

Saving of Fuel.—In the Wellner furnace the consumption of coke was from 48% to 55% in the smelting of roasted but *not* sintered ores, and from 41% to 49% in the smelting of roasted and sintered ores; whereas in the Pilz furnace it is only from 24% to 29% on the average for the sintered ores. It should, however, be stated that the coke used in the Wellner furnace was produced from the coal of the "Plauenshe Grund" near Dresden, which yielded from 18% to 25% of ash; whilst at present in the Pilz furnace Silesian coke is used almost exclusively, which yields only from 10% to 13% of ash.

Saving of Labour.—In the Wellner furnace the number of men employed was 6, and in 24 hours the largest quantity smelted was from 38 to 45 centners of roasted but *not* sintered ores, and from 65 to 70 centners of roasted sintered ores; whereas in the Pilz furnace 10 men are employed, and from 550 to 700 centners of sintered ore are smelted in 24 hours. Hence it appears that in the Pilz furnace nearly 6 times more ore is smelted per man than in the Wellner furnace.

Great Saving of Time and Expense in obtaining clean Ore Slags.—Formerly, with the Wellner furnace, these slags, in order to be made sufficiently clean, were smelted in a reverberatory furnace,

in conjunction with certain pyritic silver ores; whereas the slag produced in the Pilz furnace, after having been re-smelted in the same furnace with roasted lead-regulus, is clean enough to be thrown away, so that one of the principal smelting operations of the Freiberg process is no longer necessary. The pyritic ores, formerly smelted along with the slag in a reverberatory furnace, are now passed through a Gerstenhöfer roasting furnace, and the sulphurous acid evolved is utilized in the manufacture of sulphuric acid.

More complete Collection of Fume and Dust.—This is due to the mode of drawing off the waste-gas and fume through a pipe inserted just below the top of the furnace on one side.

Smaller Loss of Lead and Silver.—Formerly the loss of lead in ore-smelting and in regulus and slag-smelting at Freiberg amounted to from 15% to 20%, whereas now it does not exceed 2% or 4% at most; and the slags which in the former process were thrown away contained from 0·003% to 0·004% of silver, whereas those which are now thrown away do not contain more than from 0·001% to 0·0015% of silver.

Less Wear and Tear in the Furnace and Tools.—Reparation also can be more easily effected in the Pilz than in the Wellner furnace, as the former is accessible on all sides, which was not the case with the latter.

Longer Campaign.—Campaigns of the Pilz furnace have continued from 15 to 18 months, whereas the longest campaign of a Wellner furnace did not exceed 6 months.

The Pilz furnace, it should be stated, is also used in the process of desilverizing and concentrating speise, as well as in the reduction of litharge and of the skimmings produced in the softening of lead. About 2000 centners of litharge can be passed through the furnace in 24 hours.

Total Produce of the Freiberg Smelting Works (*Muldener* and *Halsbrücker Hütte*) in 1876.[8]

	lbs. (1 lb. = 0·5 kilog.)
Gold	302·22
Silver	58,430·25
	Centners. (100 ctrs. = 50 kilog.)
Soft lead, hard (antimonial) lead, stanniferous lead, litharge, and lead fume, which is used as a pigment	71,638·155
Sulphate of copper	30,804·01
Zinc and zinc dust	3765·16
Bismuth	75·50
Sulphuric acid (of 50°, 60°, and 66° B.)	185,818·57
Sulphate of iron (ferrous sulphate), inclusive of 3000 centners of sulphate of soda	17,444·80
Arsenical products, namely, red, yellow, and white glass, white arsenic in powder, and metallic arsenic	13,878·16
Shot	2224·53
Sheet-lead	3709·445
Lead pipe and wire	9674·655

[8] Akademisches Jahrbuch for 1877.

SIPHON- OR AUTOMATIC TAP.

In a paper read at a meeting of the American Institute of Mining Engineers in 1871, is the following account of what is named the siphon- or automatic tap:[9]—

"Generally a large furnace [*i.e.* blast-furnace] has two tap-holes on opposite sides, and at right angles with the front plates. One tap-hole is at the deepest point of the bottom, the other a few inches above it. Thus the metal may be tapped high or drawn off entirely, according to circumstances. Mr. Arents, of the Eureka Consolidated Works, recently made an attempt to do away with the inconvenient mode of tapping hitherto in use, and his efforts have been crowned with such success that there is not a single furnace in Eureka without this peculiar contrivance, termed the 'siphon-tap' or 'automatic tap.' It consists of a sheet-iron cylindrical shell, which is bolted on to one of the cast-iron plates, in which formerly one of the tap-holes would have been located, and 6 inches below the top of the plate. Through a hole in the side of this shell toward the furnace passes a 3-inch wrought-iron pipe into another hole in the furnace-plate, and obliquely down to the lowest part of the hearth inside. The highest point of the pipe lies in the middle of the shell, and a foot or more below its upper rim. This cylinder is rammed full of fire-clay, the pipe being meanwhile closed by a plug. A basin, 18 inches in diameter, is then cut out and the plug withdrawn. The rim of the basin is on a level about 1 inch lower than the lowest level of the matte-spout [*i.e.* channel for the outflow of regulus], which is from 3 to 4 inches below the level of the slag-spout, so that the two can be drawn off separately. During the running of the furnace the lead stands always as high in this basin as in the crucible [hearth] inside the furnace. It is proved by the actual working results, since this improvement was introduced, that (1) the furnace runs more regularly than before, (2) the lead obtained is purer, (3) 'sows' [or bears] are prevented, and (4) the work of the smelters is lightened;" and, it is added, there is also saving of fuel, because the blast is kept uninterruptedly in action, whereas in the old system it is shut off during tapping and the subsequent cleaning of the hearth, etc., operations which, it is stated, often require a considerable time, and therefore cause the temperature of the furnace to be reduced, "so that much fuel is burned to make up for lost heat."

In the arrangement above described the bottom of the hearth is *always* kept well covered with molten lead, just as in the case of the old ore-hearth in use in the North of England and Scotland; and thus contact between the substances which would form accretions and the bottom is prevented, as all such substances have a much lower specific gravity than lead. The lead flows from the bottom of

[9] The Smelting of Argentiferous Lead Ores in Nevada, Utah, and Montana. By O. H. Hahn, M.E., Anton Eilers, M.E., and R. W. Raymond, Ph.D. Bethlehem Meeting, August 1871. Transactions of the American Institute of Mining Engineers. Philadelphia, 1. p. 108.

the hearth as fast as it is reduced, on which account, it is alleged, the lead obtained must be purer, because the purest lead, being also the heaviest, subsides to the bottom, and therefore the foreign lighter metals, iron, zinc, etc., being "kept longer under the influence of the blast," are "mostly oxidized and slagged." It has been previously intimated that regulus is produced in the smelting; and if so, it might be supposed that, lying as it does between the slag and the lead, the latter could not well be exposed to the oxidizing action of the blast. The lead is laded from the receiving cavity into ingot-moulds.

In 1873, Mr. Daggett communicated a paper on smelting in Utah to the American Institute of Mining Engineers, in which he stated that "this siphon-tap is a great improvement on the old method, and Messrs. Arents and Keys, of Eureka, deserve and have the thanks of all smelters for its introduction."[1] The paper is illustrated with engravings of what is stated to be a modification of the Pilz furnace, with the siphon-tap; and in these the tap-cavity is shown to communicate with the middle of the hearth-bottom (which is rounded) by a horizontal, not inclined, channel, in a mixture of sand and clay rammed into a sheet-iron shell, as at the Eureka Works. The channel is formed by inserting, before tamping, a round piece of wood, $2\frac{1}{2}''$ or $3''$ in diameter and $3\frac{1}{2}'$ long, and having through its centre a $\frac{3}{4}''$ auger-hole. This method of forming the channel by means of a pipe of wood—for such it is—is ingenious, as it is not necessary to withdraw the piece of wood, the molten lead running through it and carbonizing it in its course. In order to remove any obstruction that may occur in the channel in the course of working, there is a small hole at the lower part of the sheet-iron shell opposite the end of the channel, through which an iron bar may be driven through the channel.

I have recently been informed by Mr. Kitchener, who is engaged at silver-smelting works at Troujes in Michoacan, Mexico, that the siphon-tap has been adopted at those works and given entire satisfaction.

Hitherto the novelty of the invention of the "siphon- or automatic tap" has not been questioned, yet that is a point which is open to doubt, as I shall now endeavour to prove. A blast-furnace having a tap-cavity on the outside, but communicating with the lower part of the hearth within, is certainly not new, if indeed it be not very old. In such furnaces the molten metal, as it dropped from above, flowed forward from the hearth into the tap-cavity, which, in reality, is only a kind of fore-hearth. In the modern invention the same thing occurs, the molten metal running into the fore-hearth through a

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[1] Economical Results of Smelting in Utah. By Ellsworth Daggett, Manager of the Winnamuck Smelting Works, Bingham Canyon, U.T. 2. p. 22. May 1873. It will be observed that in this paper the credit of the invention of the siphon-tap is divided between Mr. Arents and Keys. In a paper communicated to the American Institute of Mining Engineers, May 1875, it is stated that the siphon-tap had been adopted at the Swansea Silver Smelting and Refining Works of Chicago, 4. pp. 35 et seq.

mall channel instead of a large one as in the old furnaces. But this s merely a difference of degree and not a difference of kind, worthy f being designated an "invention;" and, if conclusive proof be equired that this is a fair statement of the case, it will be found in he engraving of a low blast-furnace, used for lead-smelting, in Karsten's Atlas to his "System der Metallurgie," No. 860, and of which a description is given in that work, vol. 5. p. 166. Karsten's engraving might, indeed, better serve as an illustration of the papers on the "siphon-tap," which have been quoted, than some of the woodcuts accompanying those papers; and as in this furnace the communication between the hearth and the tap-cavity or fore-hearth is large, it must be far less liable to be obstructed than in the American "siphon-tap" furnaces. Why the term "siphon-tap" should have been selected, I do not know; for there is nothing like the action of a siphon in the arrangement.

From the foregoing remarks it must not be supposed that I venture to disparage the use of the "siphon-tap" as a substitute for the ordinary method of tapping, in opposition to the strong testimony of American smelters in its favour. My friend Mr. Godfrey, who has had personal experience in the use of the "siphon-tap," has expressed to me the following opinion on the subject:—"When smelting can be conducted without forming accretions in the hearth, when the relative proportion of lead is considerable, and when the accompanying slag is easily fusible, the 'siphon-tap' has given satisfaction; but when tried under other conditions, it has proved a failure, and the old method of tapping has had to be resumed."

SILVER-SMELTING IN JAPAN.

For the following interesting account I am indebted to my friend Mr. J. G. H. Godfrey, lately Mining Engineer-in-chief to the Japanese Government:—

Silver ores are found in many parts of the Japanese empire. The ores most frequently met with are argentite and stephanite; ruby silver, metallic silver, and an alloy of silver and gold containing as much as about 50% of silver are also found, but are rare. Usually they are associated with sulphuretted ores, such as copper- and iron-pyrites, galena and blende, the most common vein-stuff being quartz. Rhyolite (feldspar porphyry) is the containing rock of nearly all the silver lodes; and it is only in exceptional cases that they occur in the older metamorphic rocks. The most important silver mines are in the provinces of Sado, Ugo, Rikuzen, Harima, and Hida.

In former times the treatment of silver ores was essentially the same throughout the country, but since the revolution of 1868 modern methods, varying with the nature of the ores, have been adopted in some localities. The ancient method, which is here to be described, consists of the following operations:—

I. Dressing of the ore.
II. Roasting of the dressed ore.

III. Smelting of the roasted ore with plumbiferous products.
IV. Liquation and subsequent cupellation of the argentiferous lead obtained in III.
V. Extraction of the gold from the cupelled silver by means of sulphur.

Dressing of the Ore.—The dressing of the ore is effected either by jigging the roughly broken-up stuff as at Innai (in the province of Ugo), or by washing the finely-pounded ore as at Handa (in the province of Rikuzen) and Sado.[2] Owing to the finely-divided state of the ore and to imperfection in dressing, the loss in silver is very considerable, amounting often to 50% of the assay value.

The dressed ore at Innai yields 1·4% of auriferous silver, at Sado and at Handa 1%, the proportions of gold in the auriferous silver being, respectively, 1%, 2%, and 5%.

Roasting of the Ore.—At Handa and Sado the finely-divided dressed ore is moistened with the muddy water from the ore dressing and formed into balls about 3 inches in diameter, which are dried and then roasted with small charcoal intermixed. Roasting is effected in small cylindrical kilns, having a row of small holes round the bottom for the admission of air. These kilns are made of clay, bound on the outside with hoops of wrought-iron. At Innai the ore is smelted in the raw state.

Smelting of the Ore.—The smelting is conducted in a small blast-furnace which is merely a shallow circular cavity made in the ground, the interior being lined with a moistened mixture of clay and charcoal powder. The cavity when thus lined is only 6 inches in diameter and 3 inches deep. The furnace is surmounted by a rectangular hood about 8′ high, 6′ square at the bottom, and 4′ × 2′ at the top, such as is shown in fig. 64, p. 341. The hood is made of wicker-work coated with clay. The blast is supplied by a rectangular blowing machine worked by hand, and similar in construction to that shown in fig. 207, p. 746, of the Author's volume on Iron and Steel: the dimensions of this machine are 5″ × 11″ × 2′ 4″. The blast passes through one twyer at the back and on a level with the top of the furnace. The fuel is charcoal, and the products are slag, regulus, and argentiferous lead containing copper. When the operation of smelting is finished, the incandescent charcoal is removed, and the slag afterwards skimmed off with a short round piece of dry wood attached to the pointed and bent-down end of a long iron rod, so as to form a kind of rabble. After skimming, the process of smelting is repeated as above described until the hearth becomes nearly full of regulus and lead.

In the smelting of roasted ore, the charge consists of 41·6 lbs. of ore, 8·3 lbs. of lead, and 2·5 lbs. of cast-iron. Eight of such charges are treated in one furnace per day of 12 hours. During this period all the slag resulting from these eight charges is re-smelted in the same furnace six times, each time about 42 lbs. of slag, with the

[2] The smelting works are situated near the town of Aikawa.

addition of 5·8 lbs. of lead and 0·8 lb. of cast-iron. The resulting slag, which is thrown away, contains 0·0154% (5 ozs. per ton) of silver and 0·0003% (2 dwts. per ton) of gold. For the re-smelting of the slag the hearth of the furnace is enlarged to 18″ in diameter and 6″ in depth. Each furnace yields about 51·5 lbs. of argentiferous lead per day of 12 hours with a consumption of 266 lbs. of charcoal. One smelter and one assistant are engaged at each furnace, who, besides an allowance of rice, receive 0·9*d.* and 0·7*d.* respectively, per charge. The argentiferous lead is rich in copper and has to be liquated before being cupelled. At Innai the ores are smelted in the raw or unroasted state, in a furnace of which the hearth is 10″ in diameter and 5″ in depth; and a charge is composed as follows:—

	lbs. a.v.d.
Washed ore	12·5
Regulus, from ore-smelting	2·5
Iron-pyrites (only used when the quantity of regulus is insufficient)	0·8
Litharge	3·8
Metallic lead	1·7
Slag	1·7

After the first smelting, the slag is increased to 2·5 lbs.

The consumption of charcoal is 21 lbs. per charge, and the products are 2·5 lbs. of regulus and 4·2 lbs. of argentiferous lead containing from 3% to 18% of silver, or about 10% on the average. The regulus is put back into the furnace in the next smelting. Any slag which is seen to be not "clean" is picked out to be re-smelted, and the remainder is stamped and washed in order to separate any shots of regulus or lead which it may contain. An assay of the rejected slag yielded 0·055% (18 ozs. per ton) of silver, and 0·0003% (2 dwts. per ton) of gold.

The argentiferous lead produced is cupelled without having been previously liquated. One smelter and one assistant, who receive, besides an allowance of rice, 7½*d.* and 2*d.* per shift respectively, attend each furnace; and during a 12-hour shift, according to the supply of ore, from 8 to 15 charges are passed through the furnace.

Liquation of the Argentiferous Lead.—The lead resulting from the smelting of roasted ore contains a considerable amount of copper, and consequently has to be liquated. Liquation is effected in a small furnace such as is shown in fig. 64, p. 341. In each furnace 60 lbs. of lead are liquated per day of 12 hours with a consumption of 100 lbs. of charcoal. The products are 51·7 lbs. of silver-lead and 8·3 lbs. of residual copper, which is sold to copper refineries. Each furnace is attended by one man and one woman, who receive 3½*d.* and 2*d.* per shift, respectively, in addition to an allowance of rice for food.

Cupellation.—Cupellation is conducted on small tests made of wood-ashes. One charge weighs 6·7 lbs., and is cupelled in about 1½ hour. Eight of such charges are cupelled per shift of 12 hours, and each furnace is superintended only by one woman, who is paid

2*d.* per day, besides an allowance of rice; the daily consumption of charcoal is stated to be 21·7 lbs., and that of wood-ashes 133 lbs. per furnace. A test is thus prepared:—A quantity of wood-ashes is piled up on the ground, and beaten solid and flat at the top. In this heap a circular dish-shaped cavity is fashioned by striking with a bag filled with the ashes of straw. The ashes are cut away round the rim of the cavity, and segments of burnt clay are inserted in their place, thus forming a flat ring of clay at the top of the cavity, as otherwise it would be easily injured. The blast is produced from an ordinary Japanese rectangular box-like blowing machine, of which the dimensions are 20″ × 12″ × 5″. The products of these eight charges are as follow: silver, and 53·3 lbs. of litharge, which is reduced by heating it with charcoal, and from which only 36·2 lbs. of lead are obtained.

The cupellation of the argentiferous lead comprises two processes: the first in which only imperfectly refined silver, similar to the "Blicksilber" of the Germans, is obtained; and the second in which fine silver is produced. In the first process, when poor lead (*i.e.* lead such as is produced in lead-ore smelting, and containing 0·2% of silver) is the subject of treatment, three cupellations are required, and in the last, instead of the blast from the blowing machine, a man blows upon the metal through a bamboo pipe; but in the case of rich lead one cupellation suffices, and no mention is made of the use of the mouth-blast. During the first two cupellations, when the furnace is attended by one smelter and one woman, a piece of square iron is laid over the test in the direction of the blast, and other pieces are laid at right angles, the object of which arrangement is to support the ignited charcoal. When the mouth-blast is used, one long piece of charcoal supports all the other pieces, which lean against it and the sides of the test. The loss of lead in this process, inclusive of that which occurs in the reduction of the litharge, is 23% of the total lead used.

It should be stated that the charge of argentiferous lead for cupelling varies from 4 to 50 lbs., according to the richness of the lead in silver: the richer the lead the smaller is the charge; and the time occupied in the process increases with the quantity of the charge, and varies from ¾ of an hour to 2 hours. The consumption of fuel, on the average, is 40% of the weight of the charge.

The second process, in which the silver is made fine, is conducted on a test 8″ in diameter, surmounted by a bell-shaped vessel of cast-iron, which is open at the top and forms a chamber for the fuel. The charge consists of from 17 to 21 lbs. of imperfectly refined silver from the first process and 2½ lbs. of lead; and the process is completed in 3 hours with a consumption of 42 lbs. of charcoal. The yield of refined silver is 99% of the imperfectly refined silver; and the litharge obtained amounts to 2·7 lbs. This litharge is heated with charcoal, and the reduced lead yields by cupellation 0·01 lb. of silver.

Extraction of the Gold from the Silver by Sulphur.—The extraction of gold from the imperfectly refined silver is effected by repeatedly melting the latter with sulphur and subsequent partial

reduction of the resulting sulphuretted product. This product contains most of the silver and some gold, and the small amount of unsulphuretted metal most of the gold. The silver is extracted from the sulphuretted product by melting the latter and exposing it while molten to the action of a blast of air.

In nine furnaces, of which three are used for melting the auriferous silver with sulphur, three for blowing off the sulphur, and three for cupelling, 15 lbs. of the silver are treated per day of 12 hours, yielding 0·58 lb. of enriched auriferous metal and 14·07 lbs. of silver.

All these furnaces are similar in construction to those described under smelting and cupelling; and in their management are employed 6 smelters and 6 blowers, who, besides an allowance of rice, receive each, respectively, 4½*d.* and 3½*d.* per day of 12 hours. The quantity and cost of materials used in the treatment of the amount of cupelled silver above stated are as follow :—

Charcoal, 17½ bags, containing each 32½ lbs. (of which 0·0301 dollar worth is consumed in the warming of the fingers of the superintending officials!)	$1·0943
Sulphur, 17 lbs.	0·3996
Wood-ashes, 54 lbs.	0·0650
Old copper, 0·15 lb.[1]	0·0209
Lead, 18 lbs.	0·8895
Wear and tear of tools per day	0·2362
Total	$2·7055

In 1872 the average price of 100 lbs. of charcoal was 9·1*d.*, 9·6*d.*, and 18·0*d.* at Sado, Innai, and Handa, respectively.

The gold obtained by this process still contains a considerable quantity of silver, from which it is freed by repeatedly cementing it, in a granulated form, with common sea-salt in clay dishes, each cementation lasting about 24 hours. For the treatment of 0·32 lb. of argentiferous gold are required 62·5 lbs. of salt and 167 lbs. of charcoal; one foreman and 2 labourers being employed in this operation. The yield of cemented gold from the quantity of argentiferous gold above stated is 0·095 lb. The cementing mixture is washed with water, and the residue, which contains the silver as chloride, weighs 4·2 lbs. From this residue 0·174 lb. of silver is obtained by fusion with the addition of 1·7 lb. of metallic lead, and cupelling the resulting argentiferous lead, the consumption of charcoal in both operations amounting to 41·6 lbs. The sweepings, from the treatment of the cupelled silver with sulphur, the quantity of which is considerable, are concentrated by washing, and the product is smelted with the addition of lead and litharge. The lead thus obtained is cupelled; and the slag formed in this operation is broken up small and washed, the heavy portion thus separated being afterwards treated in the same way as the concentrated sweepings, and the remainder thrown away.

[1] It is difficult to conceive how so small a quantity of copper should produce any sensible effect, yet the reason assigned for its use is that it acts as a flux.

SMELTING OF GALENA, RICH IN SILVER AND ASSOCIATED WITH PYRITIC AND ARSENICAL MINERALS, IN THE PROVINCE OF OMI, JAPAN.

As information concerning smelting processes of a more or less primitive character are always interesting to the scientific metallurgist, especially from an historical point of view, I have pleasure in here presenting another description of silver-smelting in Japan, for which I am indebted to my friend and former pupil, Mr. William Gowland, chemist and metallurgist to the Mint at Osaka in Japan. For some years Mr. Gowland was engaged in copper-refining at the Broughton Copper Works near Manchester, where he made numerous and elaborate analyses of the varieties of copper occurring in commerce, investigations respecting their electric conductivity, and many original observations, especially on the subject of "poling." From my knowledge of Mr. Gowland, I can with confidence assert that, in my opinion, no one could be more competent than he accurately to describe a metallurgical process. The following description, which is founded on personal inspection, was communicated to me for publication in 1873:—

Description of the Mine.—The mine was worked by levels driven in the side of the hill, and the water got rid of by an adit. These levels were driven entirely at random, no system being followed, excepting that when an ore-bearing part was reached it was followed up until it ceased. There were native plans of the mine, but these gave no accurate information either as to the direction or extent of the workings. In the harder parts the levels were carried forward with the aid of gunpowder. The vein, which was very wide, dipped at a high angle, and was chiefly filled with a blue shale, the ore usually occurring in this in thin straggling veins, and in "pockets very irregularly. Similar veins of calc spar also occurred freely. The "country" rock consisted of a silicious shale, much decomposed, broken up and weathered at the surface.

Nature of the Ore.—The ore was galena with a large intermixture of mispickel, iron- and arsenical pyrites, and occasionally also of copper-pyrites. (In a foot-note Mr. Gowland states that this was the material smelted at the time of his visit, but that since then, in 1874, a vein of galena had been discovered about 10′ thick and of moderately high produce.) It was very poor in lead, the roasted ore only yielding from 4% to 5% of lead, from which however 0·8% of silver was obtained.

Fuel.—This consisted of wood for the roasting kilns and of charcoal for the smelting furnaces. The hill-sides were covered with magnificent trees of *Cryptomeria* (a genus of the family *Pinaceæ*); but as here, as well as at several other mining districts in Japan visited by Mr. Gowland, the trees were cut down wholesale and no attempt made to replace them by planting, there must, of necessity, soon be such a scarcity that timber will have to be procured from other districts. The charcoal used was that of the oak, maple, and *Retini-*

spora obtusa (also a genus of the family *Pinaceæ*), that from the *Cryptomeria* being disliked, as it was said to be soft and swift-burning.

Roasting.—Roasting is effected in kilns which are square, 4′ wide and 4′ deep, and are quite open at the top. Their sides are rudely built of stone and clay, and usually there are four, six, or even more kilns side by side in a row. At the bottom of the front side there is a hole which is opened or closed when necessary, according to the rate of the combustion. The ore, having been previously broken up by hand into pieces about the size of small walnuts, is piled in the kilns with wood in alternate layers. The roasting lasts for five days, after which the partially roasted ore is removed to an adjacent kiln, in every respect the same as above described, and roasted in the same way and during the same time as at first. Even after this second operation the ore was but imperfectly roasted, the fracture of the pieces often showing unaltered ore in the interior.

Smelting Furnace.—This is situated under a rude chimney of bamboo wicker-work thickly coated over with clay. It is not really a chimney but a hood, being open on the front side to about the height of 6′ from the ground, where it is fully 6′ wide. Its back-wall screens the men who work the blowing machines from the heat of the furnace, of which machines there are two placed behind this back-wall. The furnace itself is merely a more or less hemispherical cavity in the ground, lined with a refractory clay (an impure kaolin, of which there is an inexhaustible quantity in Japan). It is 18″ in diam., from 12″ to 14″ deep, and is half covered by a semicircular lid of clay 4″ or 5″ in thickness. Below this lid, at the back of the furnace, are two apertures by which the blast is admitted. The blast is conveyed to these apertures by clay tubes running just below the surface of the ground, and the ends of which near the furnace incline a little downwards. The blowing machines are of the ordinary Japanese form. The furnace is re-lined after each day's work, but the lid is only renewed occasionally. A furnace identical with this is used in Osaka in silver refineries for smelting the saturated ash-bottoms of the cupelling furnaces.

Charge, Management of the Furnace, and Yield.—The daily charge was 600 lbs. of calcined ore, divided into four parcels of 150 lbs. each, one parcel being charged into the furnace every 1½ hour, and the whole worked off in about 6 hours. The entire charge of 600 lbs. only yielded on an average from 25 to 30 lbs. of lead, which however contained 0·8% of silver. The furnace having been re-lined and carefully dried after the work of the preceding day, the lid having been fixed so as to half-cover the top and a small quantity of ignited charcoal being already in the furnace, a quantity of charcoal, a little less in volume than a parcel of 150 lbs. of ore, was put into the furnace and heaped up above the open half. On the top of the charcoal the calcined ore was spread so as to cover it uniformly and entirely. The heap was then gently patted with a small flat iron tool, and the blowing machine set to work gently. Very soon blue jets of ignited carbonic oxide began to make their appearance, and in a short time

were seen to issue from over the whole surface of the pile, the workman patting the heap from time to time to prevent the formation of hollow places and keep the jets of flame as uniform as possible in every part. This he succeeded in doing most successfully; and, the heap gradually becoming less and less in volume, in about 1½ hour the whole mass had subsided into the furnace-cavity, which mass then consisted chiefly of slag, with some regulus, a little metal, and unconsumed charcoal. The unconsumed charcoal was now removed, the slag raked off with a wooden rake, but the regulus and metal were allowed to remain. The slag was black, well melted and very clean, it being difficult to detect shots of regulus in it. Another charge of charcoal was placed on the top of the regulus and metal, another parcel of 150 lbs. of ore spread over it as above described, and the same treatment followed and repeated twice more, when the whole charge of 600 lbs. of ore will have been smelted. When the slag from the last smelting has been removed, the clay lid of the furnace is taken off, and a little water is thrown upon the regulus, which is then removed in cakes, as in the process of making "rosette copper" in Europe. The lead was next laded out with a shallow ladle and poured into a small hollow in the floor near the side of the furnace. The regulus was roasted, and was added to a charge of ore in a subsequent smelting. Although Mr. Gowland had no opportunity of assaying the ore treated, yet he considers that the loss of lead must have been very great. During the whole operation of smelting volumes of dense white smoke were given off, and so much arsenical fume that it was surprising that no cases of poisoning had occurred. It was stated that, in the smelting of richer ore, scrap-iron was mixed with the charge, and that the lead and regulus were removed every second heat; that is to say, after 300 lbs., or two parcels of ore, had been smelted. After Mr. Gowland's visit, he ascertained that the rich galena previously mentioned in a note in the text, p. 556, had been smelted in the same kind of furnace as above described, but that the total yield only amounted to 40% of lead, though a sample of this ore assayed by him in the iron crucible yielded 69% of lead and 125 ozs. 8 dwts. of silver per ton of ore.

AMALGAMATION OR THE EXTRACTION OF SILVER FROM ITS ORES BY MEANS OF MERCURY.

There are various processes for the extraction of silver from its ores by means of mercury, and the general expression by which they are designated in metallurgical language is that of amalgamation. The date of the first use of mercury for this purpose is unknown. That gold might be separated from certain impurities by mercury was known to the Romans, as is shown in the following extract from Pliny:—"Omnia ei [i.e., argento vivo] innatant præter aurum; id unum ad se trahit. Ideo et optume purgat, ceteras eius sordis exspuens crebro iactatu fictilibus in vasis; ita autem iis eiectis, ut et ipsum ab auro discedat, in pellis[es] subactas effunditur, per quas sudoris vice defluens purum relinquit aurum."[1] [Everything floats upon it [quicksilver] except gold; that alone it attracts to itself, and therefore best cleanses, expelling the rest of its impurities by repeated shaking in earthen vessels; these being thus ejected, in order that it itself may leave the gold, it [*i.e.*, the amalgam] is poured into skins [that are then] squeezed, through which exuding like sweat it leaves the gold pure.]

It should be particularly noted that gold is stated to be the *only* substance which mercury attracts to itself, and that no reference is made to silver, for which it has a very strong, though, it may be, not an equally powerful, attraction.

It is hardly necessary to remind the reader that by this treatment the gold would be left, not pure, but in the state of solid amalgam. In the preceding passage from Pliny there is certainly no intimation that silver might, like gold, be separated from impurities by means of mercury, though Beckmann quotes the same passage as his authority for a contrary statement;[2] and I have not found any such intimation in any other part of Pliny's treatise.

The earliest account of the use of mercury in the metallurgy of silver which I have met with is that in Biringuccio's treatise in Italian published in 1540, and it is remarkable that it should have been overlooked by Beckmann, who makes no mention of it in an article on "Refining Gold and Silver Ore by Quicksilver" in his learned work on the History of Inventions. This account is so interesting from an historical point of view that I cannot refrain from presenting the following literal translation of it *in extenso*:[3]—

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[1] Naturalis Historiæ Lib. xxx. cap. vi. sect. 32. Sillig's edition. 1851. 5. p. 100.

[2] A History of Inventions and Discoveries. Trans. 2nd ed. London, 1814. 1. p. 24.

[3] Being desirous of having an authoritative translation of this account, I applied to Mr. George Bullen, in the Library Department of the British Museum, who was kind enough to obtain one for me from his colleague, Mr. E. A. Roy. I have also received an admirable translation of this and other parts of Biringuccio's treatise bearing upon the subject from my friend Mr. A. Dick, who has very carefully studied the whole treatise in the original Italian. The translations of Mr. Roy and Mr. Dick agree in every essential particular.

"*Method of extracting all Substances of Silver or Gold from the Refuse of Ores or from the Sweepings of Mints, of Goldbeaters or Goldsmiths, and also of extracting the Substance which certain Ores contain.*

"He was certainly endowed with much useful and ingenious thought who invented the short method of extracting metal from the sweepings produced by those arts which have to do with gold and silver, every substance left in the refuse by smelters, and also the substance from certain ores themselves, without the labour of fusing, but by the sole means and virtue of mercury. To effect this a large basin is first constructed of stone or timber and walled, into which is fitted a millstone made to turn like that of a mill. Into the hollow of this basin is placed matter containing gold (*della materia vra che tiene oro*), well ground in a mortar and afterwards washed and dried; and, with the above-mentioned millstone, it is ground while being moistened with vinegar, or water in which has been dissolved corrosive sublimate (*solimato*), verdigris (*verde rame*), and common salt. Over these materials is then put as much mercury as will cover them; they are then stirred, for an hour or two, by turning the millstone, either by hand- or horse-power, according to the plan adopted, bearing in mind that the more the mercury and the materials are bruised together, by the millstone, the more the mercury may be trusted to have taken up the substance which the materials contain. The mercury, in this condition, can then be separated from the earthy matter by a sieve, or by washing, and thus you will recover the auriferous mercury (*el vro mercurio*). After this, by driving off the mercury by means of a flask [*i.e.* by heating in a retort or an alembic], or by passing it through a bag, there will remain, at the bottom, the gold, silver, or copper, or whatever metal was placed in the basin under the millstone to be ground.

"Having been desirous of knowing this secret, I gave, to him who taught it to me, a ring with a diamond worth 25 ducats; he also required me to give him the eighth part of any profit I might make by using it. This I wished to tell you, not that you should return the ducats to me for teaching you the secret, but in order that you should esteem it all the more and hold it dear."[4]

The preceding account by Biringuccio is illustrated by a woodcut in which two mills are shown, resembling a common flour-mill: in one the upper stone or runner is turned by a man pushing an arm attached at right angles to the vertical shaft; while in the other there is a crank on the shaft by which rotation is effected also by one man.

In an earlier part of his treatise, in a chapter devoted to the preparation of ores, Biringuccio states that they may be ultimately worked either on a bath of lead or by means of mercury. He next describes the treatment of ores "which are pure;" but what these ores were does not appear. It is, however, clear that they were not

[4] "De la Pirotechnia . . . per . . . Vanoccio Biringuccio, Sennese. Venetia, 1540." Lib. ix. cap. xi. fol. 142.

ores containing native silver; for he says he had never seen native silver, but believed it might occur in mines, because he had seen native copper, and read in "one George Agricola, a German," that the Duke of Saxony was proud of having a table made of native silver. The account of this table is given in Agricola's "Bermannus," first published in 1528.[5]

Concerning those minerals of silver "which are pure," Biringuccio writes as follows:—

"Preparing them as I have told you (*i.e.* roasting, quenching in water, grinding and washing on sieves, etc.), and then washing them and afterwards drenching them with vinegar in which has been put green copper (*i.e.* verdigris); or drenching them with water in which has been dissolved vitriol and green copper. . . ."[6] He next describes how the ores, which have been thus rendered "pure," should be ground with mercury, in the manner stated with more detail in his subsequent description, of which the translation has been given above; but only in the former does he mention the use of vitriol and the nature of the material, deerskin leather, of which the bag for filtering the amalgam should be made.

By *solimato* corrosive sublimate is clearly intended, as may be inferred from other passages in Biringuccio's treatise in which the method of preparing that substance is described; by "vitriol" is meant green-vitriol or ferrous sulphate, the preparation of which he also describes elsewhere in the same treatise; and "green copper" seems in most cases to mean verdigris.

There are other passages in Biringuccio's treatise in which he alludes to amalgamation. He also shortly describes the old method of assaying silver ores with mercury,[7] which does not differ in principle from the process of amalgamation, except when the ores are "hard and savage;" in which case they are to be calcined once or twice before treatment with mercury, and, if they do not then give up their silver, the assay is to be made with lead.

It has generally been admitted that in 1557 Bartolomé Medina, a miner at Pachuca in Mexico, invented the process of extracting silver from its ores by means of mercury in admixture with certain other substances, or, as it is usually designated, the Mexican Amalgamation or Patio process. It is stated that the oldest documents in which it is mentioned are a report addressed to the Viceroy of Mexico (de Sarria states, the Viceroy of Peru), by Luis Berrio de Montalvo, printed in the city of Mexico in 1643, and a memoir by Diaz de la Calle to Philip IV., printed in Madrid in 1646, in both of which Medina is recorded as the inventor of the process.[8]

This statement as to the first publication of the process is certainly not correct; for, according to Don Joseph Garces y Eguia, the first printed treatise on Amalgamation as then conducted is that

[5] Georg Agrikola's Bermannus . . . übersezt von Friedrich August Schmid. 1806. p. 32. The account of the silver table is at p. 150 of this edition.

[6] Op. cit. folio 48.

[7] Op. cit. folio 45.

[8] St. Clair Duport, op. cit. p. 49.

of Barba, published in Peru in 1639.[9] The process was introduced into Peru in 1571 by Pedro Fernandez de Velasco, and still continues to be practised there.

The foregoing extracts from Biringuccio's treatise, published in 1540, prove conclusively that a process very similar, in certain respects, to the Mexican, was known and practised in Europe at least seventeen years before 1557; and as it was communicated to Biringuccio as a valuable secret, for which he paid what would be considered a high price in those days, it is probable that it was in operation in Europe even long anterior to 1540. It is not impossible that Medina may have independently invented the process, yet it seems to me more reasonable to suppose that a knowledge of it was obtained by the Spaniards from Europe, and conveyed by them to Mexico. Indeed, it is asserted by Berrio de Montalvo that Medina had "heard in Spain that with mercury and common salt the silver might be extracted from minerals for which no smelting process could be found" (Ensayo de Metalurgia, by Don Francisco Xavier de Sarria. Printed in Mexico, 1784).

The points of similarity in the process described by Biringuccio and the Mexican are the use of mercury in conjunction with common salt and a salt of copper, without the use of fuel except for expelling mercury from the pressed amalgam; and the difference between them consists mainly in the mode of manipulation.

In the amalgamation of silversmiths' sweep, which contains metallic silver, either free or in the state of alloy, corrosive sublimate may possibly facilitate amalgamation by attacking the metallic particles and forming a coat of amalgam on their surface. The use of vitriol (ferrous sulphate) is only mentioned by Biringuccio in his first or abridged account of the process, so that he does not seem to have regarded it as essential.

The order in which the processes of amalgamation will be described is founded mainly on the chemical state in which the silver exists in the ores; but it is difficult, if not impossible, to follow that order with absolute precision, because most of the ores which are treated by amalgamation contain silver in more than one state. Silver ores may, with reference to amalgamation, be divided into three classes: I. in which the silver exists mainly in the metallic state; II. in which it exists mainly in the state of simple and complex sulphides, inclusive of antimonial and arsenical sulphides, and which may be designated sulphuretted ores; and III. in which it exists in combination with chlorine, bromine, or iodine.

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[9] Nueva Teórica y Práctica del Beneficio de los Metales de Oro y Plata. By Don Joseph Garces y Eguia. Mexico, 1802. p. 79. The first edition of Barba's treatise, which was published in Europe, is dated Madrid, 1640. Don Luis Berrio de Montalvo wrote a treatise on Amalgamation which he published in 1643, in the city of Mexico. A treatise on the same subject, by Don Felipe de la Torre Barrio y Lima, was published in 1738 in Lima, and another by Don Juan de Ordoñez was published in Mexico in 1758. The authority for these notices is the author of the volume above quoted, pp. 79–81.

AMALGAMATION OF ORES OR OTHER SUBSTANCES IN WHICH THE SILVER IS PRESENT IN THE METALLIC STATE.

Ancient Method of amalgamating Ores rich in Native Silver in Peru.

The following information on this subject is derived from Barba's treatise, published in 1640.[1] *Machadado* is the name applied to ores containing visible native silver or gold. Such ores cannot well be ground, and mercury will not take up those metals when they are in thick pieces; and, moreover, they are difficult to smelt, on account of the dryness [*i.e.*, want of liquidity at a high temperature] of the intermixed rock, which could not be separated without risk of much loss.

These ores are treated in what is termed the Tintin process, which is also applicable to all other ores, in which, after calcination, grains of silver or gold may be perceived, especially those containing crude silver in greater or less quantity. The apparatus used in this process is thus described by Barba:—A circular, mortar-like cavity, about 9″ wide or more at the top and of the same depth, is made in a hard stone. In this cavity the ore, in small pieces, is triturated with mercury under water, an iron pestle being used for the purpose. During the operation a small stream of water is kept constantly flowing into the cavity at one side at the top, and out on the opposite side also at the top. The escaping water, rendered muddy by fine suspended particles, runs into tanks, where, on standing, those particles are deposited; and if the ore contained any brittle compound of silver or other metal, not acted upon by mercury, it will be found in the deposit, which in that case is reserved for treatment by the Patio process, to be described in the sequel. The silver and gold existing in the metallic state in the ore are taken up by the mercury, forming amalgam, from which they are extracted in the usual manner hereafter to be described.

Barba mentions two other machines for grinding ores—one named *trapiche* and the other *maray*. They are used at the mines of Peru where there is no water for driving mills, and not sufficient silver to pay the expense of constructing such mills.

The *trapiche*, or, as it is frequently termed, the Chilean mill, is similar in construction to the edge-runner mill of the present time, which is commonly used for grinding and mixing mortar and for many other purposes, and which, Barba states, resembled the mill for crushing olives. In the Peruvian *trapiche* there was only one runner, which was made of hard stone, as was also the bed. The mill was driven by horses or mules.

The following excellent account of the *trapiche* is given by Miers:[2]—"The *trapiche*, or mill for grinding the ores of gold and silver, is a very simple and rude piece of mechanism. Its moving power is constructed after the same fashion as the mills used through-

[1] Arte de los Metales, antea cit. lib. iii. cap. 16.

[2] Travels in Chile and La Plata. By John Miers. 2 vols. 1826. 2. *p. 390.* This work contains much matter of interest to the metallurgist, and is illustrated with lithographs from drawings by the author.

out Chile, and in some parts of Spain and France, for grinding corn; that is to say, a place is chosen where a small current of water, whose section will present a surface of 6″ in diameter, can be brought to a spot where it can fall perpendicularly 10′ or 12′. At this place a well is built of this depth about 6′ in diameter; in its centre is fixed an upright shaft, upon a central brass pin; it is confined above by a wooden collar. A little above its foot the shaft has affixed to it a small wheel, around which are fixed a number of radiating spokes shaped at the ends somewhat like hollow cups, and forming, in the whole, a kind of horizontal wheel 4′ in diameter. Upon the periphery of the cups the jet of water is made to impinge with all the force it has acquired in falling down an inclined and nearly perpendicular trough, formed by scooping out the solid trunk of a tree. The application of this force causes the wheel to revolve with a quick rotatory motion. The arm extends about 6′ above the top of the well, and at about half this height is fixed a small horizontal arm, 4′ long, which serves as an axle to a ponderous stone of granite, whose diameter is from 4′ to 6′, and which is thus made to roll upon its edge in a circular trough sometimes made of granite, sometimes of hard wood. The weight of this stone, assisted by its velocity, effects the pulverization of the ore. In some cases it is taken out in the dry state, and subjected to the application of sifting, in order to separate the finer powder for amalgamation, and the coarser parts are thrown again into the mill; but more generally, in order to save labour, this separation is accomplished by the action of water. For this purpose a small stream is made to trickle into the annular trough, by which means the pounded ore is mixed into a state of mud, the finer particles being sufficiently attenuated to run off with the superfluous water, through a notch made for the purpose in the margin of the circular trough. This is received in little pools, where the pounded ore is left to settle. The clear water is run off, leaving the powder at the bottom to be taken to the place of amalgamation."

The *maray* is a very simple and primitive contrivance, of which Barba gives only a very short account, alleging as the reason that it was too well known to need description. This machine was in use in Chile for triturating gold ore in the first quarter of the present century, and is probably still in operation there. The best description of it that I have met with is the following by Miers,[3] who designates it a kind of *trapiche*. "It is formed of two stones, the under stone being about 3′ in diameter and slightly concave. The upper stone is a large spherical boulder of syenitic granite, about 2′ in diameter, having on its upper part two iron plugs fixed oppositely, to which is secured, by lashings of hide, a transverse pole of canelo wood, about 10′ long. Two men, seated on the extremities of this lever, work it up and down alternately [just like two lads playing at see-saw], so as to give to the stone a rolling motion, which is sufficient to crush and grind the materials placed beneath it."

[3] Op. cit. 2. p. 398.

Barba states that the *machadado* is ground in this machine along
h the mercury and water, which is kept running in and out as in
tintin and *trapiche*. The finely-ground stuff, which is carried off
the water, is also collected and treated in the same manner as that
n the Tintin process.

Ancient Method of amalgamating in Norway.

Schlüter states in his treatise published in 1738 that the ore of
ıgsberg in Norway, which, it will be remembered, consists chiefly
ıetallic silver, was treated by amalgamation; and that in various
ns in Germany gold and silver were extracted from the "sweep"
nints and goldsmiths' workshops by the same means, especially
ere smelting works were too distant, or when there was not a
icient quantity to make it profitable to send it thither. The dis-
antages of amalgamation he considered to be the costliness of the
cury, the loss of nearly half of it in the process, the laboriousness
he manipulation when the mill was worked by hand, and the loss
ıot less than from 2 to 3 loths of the precious metals per centner
he residues, even when the process was very well conducted.

The following description is given by Schlüter of the amalgamation
ls which were used at Kongsberg, and were driven by water-power;
in the original it is illustrated by engravings, of which I have
e only reproduced the essential portion (fig. 85). It consists of a

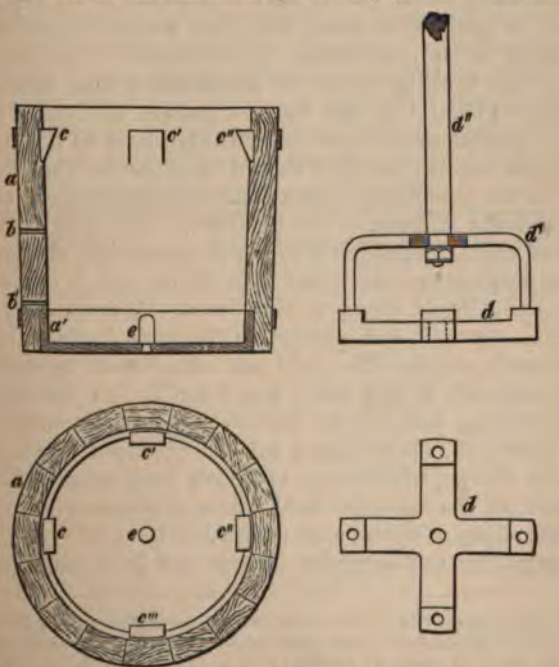

Fig. 85. Norwegian Amalgamation Mill. Drawn by Mr. W. Prim from the engraving in Schlüter's treatise. Scale of about $\frac{1}{2}''$ to $1'$.

ooden tub. *a'*. Cast-iron pan. *b*, *b'*. Tapping holes. *c*, *c'*, *c''*, *c'''*. Brackets to support the cover.
l. Cast-iron cross. *d'*. Driving fork. *d''*. Spindle. *e*. Pivot or centre. In the original it is
ot stated whether the pivot formed part of the casting or not. The shading at the top of *d''* and
here the latter passes through *d'* should have been in oblique lines, as in the usual sectional shading.

shallow cylindrical pan of cast-iron, with a flat bottom, in the centre of which is a pivot; and of a cross-shaped piece of cast-iron, having four equal arms at right angles to the axis, and a hole through the centre. The cross is placed in the pan, so that the pivot passes through the hole in the centre of the cross. The cross should fit accurately into the bottom of the pan, with the ends of its arms nearly touching the sides. The pan is surmounted by a wooden tub, of which it forms the bottom; and it is let in so that the inner surface of the sides of the pan is flush with that of the sides of the tub. To the cross is fixed an iron spindle having two fork-like prongs at the bottom, the ends of which fit into the ends of two opposite arms of the cross respectively,[4] while on the upper part of the spindle there is a pinion by which rotation is caused by means of a large horizontal crown-wheel. In the engraving 18 of these amalgamation mills are shown arranged round one such crown-wheel. In the front of each tub there are 2 or 3 holes above each other in the same line, through which the muddy liquid from within may be drawn off at different levels. During the working of the mill the tub is covered over at the top. It should be stated that there were single mills which might be worked by one man at a time, though, as the labour was great, it was advisable to employ 2 or 3 men, in order that they might relieve each other at short intervals.

The substances containing metallic gold or silver, which it is intended to amalgamate, should first be stamped or triturated, if they are coarser in grain than sand, and then washed in order to reduce their bulk, as far as practicable, by the removal of non-metalliferous matter, so that nothing coarse or unnecessary may enter the mill. About two "Tröge"[5] of the washed residue are thrown into the mill, water poured upon it, and afterwards about 40 lbs. of mercury. Grinding now begins; and if it should be perceived that the mill will take more of the washed substance, some is added along with sufficient water to prevent stiffness of the mixture. The working of the mill is continued until the residue is brought wholly into the state of mud, and when this occurs the upper hole in the tub is opened to draw off the muddy liquid down to that level. A fresh charge is now thrown into the mill, and ground to the same degree of fineness as that previously added. The gold and silver pass together into the mercury, rendering it very stiff; and when it has become so stiff as to make grinding difficult, the mill is stopped, the muddy liquor or slime is drawn off, the amalgam taken out, wiped clean, and dried. Any of the charge, which may not have been ground fine enough, settles down on the amalgam in the state of coarse powder, and must be reground along with the next charge.

The clean and dry amalgam is squeezed in a calf-skin bag, and

[4] In the engraving only two prongs are shown, but there appears to have been provision for four, as may be inferred from the holes in the ends of the arms of the cross.

[5] "Trog" (plural Tröge) is a measure, which according to the French translation bearing Hellot's name, though made by a German metallurgist resident in France, was equivalent to from 40 to 50 lbs.

what remains in the bag is heated in a retort until the mercury has been driven off, after which the retort is broken, the silver taken out, and melted. The mercury which has been strained through retains some silver, and gold also when the amalgam is auriferous.

In the amalgamation of "sweep" smaller mills may be used, but the method of proceeding is the same as that above described.[6]

The Tina System of Silver Amalgamation as practised in Chile.

I am indebted to my friend the late Mr. David Forbes, F.R.S., for the following excellent description, which he himself corrected in type.

This process, which is but a modification of the old and long-abandoned Norwegian method of amalgamation, is also known in Chile as the "Sistema de Cooper," from the name of its introducer into that country. Although only suited to the treatment of such silver ores as admit of direct amalgamation, it has nevertheless been during the last quarter of a century successfully employed on an extensive scale, especially in the north of Chile; and many large amalgamating establishments, such as the Maquinas de Gallo, Codicido, Abbot, Transito, Ossa, Echevarria, Mandiola, Cousiño, and others, situated along the valley of the Rio de Copiapó, were in active operation during my residence in that part of South America.

Owing to the present large production of silver ores unsuited for direct amalgamation, and the recent introduction of a new system of amalgamation appropriate for the treatment of such ores, it is difficult if not impossible to ascertain the total amount of silver ores annually amalgamated by this process of late years, but the following statement shows the quantity of silver ore treated, and the fine silver produced, in five of the Copiapó establishments during the thirty months from January 1, 1851, to June 30, 1853.

Name of works.	Ore reduced in quintals of 100 lbs.	Fine silver produced in lbs.
Cerillos	69,575·47	80,789·76
Ossa	27,726·13	67,635·54
Transito	33,595·56	49,155·56
Punta del Cobre	4,969·82	1,387·00
Pabellon	15,956·51	31,816·45
	151,823·49	230,784·31

It may also be mentioned, that during the same year (1853) the entire production of the Copiapó silver amalgamating works, as reported to the Government, was 164,098·5 lbs. fine silver, valued at about £639,984; whilst, in the same year, the quantity of so-called "minerales frios," or silver ores unsuited for direct amalgamation, and consequently exported to Europe (chiefly to England), was about 58,480 tons, valued on the spot at £350,885.

[6] *Gründlicher Unterricht*, antea cit. pp. 211 et seq.

DESCRIPTION OF THE ORES.

The silver ores of the north of Chile are all obtained from lodes traversing the Upper Oolite, in close proximity to the eruptions of diorite which have disturbed these strata; the matrix is usually very calcareous, and on this account the ores are found to be less suited for treatment by the Freiberg system of amalgamation, since they cause the formation of much sulphate of lime in the barrels.

The silver occurs principally in the native state or combined with mercury, as arquerite, amalgam, and several other compounds, which have been described by Domeyko; as chloride and chlorobromide of silver in very large quantity, and as sulphide of silver; and, in some of the mines, bromide and iodide of silver and bismuthic silver also present themselves.

Of late years, however, since many of the mines have become deeper (in the Colorado mine at Chañarcillo a depth of some 300 fathoms has now been attained), the characters of the ores in depth have altogether changed: the chloride, chlorobromide, bromide, and iodide, are no longer found; but, instead of them, large quantities of sulphides, sulpharsenides, and sulphantimonides make their appearance, the prevailing ores found in depth being, besides native silver, silverglance or argentite, proustite, pyrargyrite, and polybasite.

These latter ores, which are called by the miners "minerales" or "metales frios," being unfit for treatment by direct amalgamation, have in greater part been exported to Europe (until within the last three years, when a new and successful mode of treatment has been introduced, by which they are now all treated in Chile); whilst the others, called in contradistinction "minerales" or "metales calidos," are amalgamated by the Tina process about to be described.

DESCRIPTION OF THE MACHINERY.

The silver ore, as it comes from the mines, is received at the works in fragments of about half to three-quarters of a cubical inch, and is then ground to fine powder under the so-called Chilean mills, which are vertical or edge-runners, from 4 to 6 feet in diameter, formed usually of stone surrounded by an iron rim, each runner weighing about 4 tons.

The ground ore is then amalgamated in *tinas* (tubs or vats), such as are represented, both in plan and section, in figs. 86, 87, and 88. The *tinas* are wooden tubs, somewhat less in diameter across the mouth than at the bottom, formed of staves about 2¼ inches thick and 3 feet in height, held together by three iron hoops, 2¾ inches broad and from ⅛ to ⅜ inch in thickness. The internal diameter of the *tinas* varies at different establishments, from 5 to 6 feet at the bottom and about 6 inches less at the mouth.

The bottom is formed by a single circular plate of cast-iron, of a diameter corresponding to that of the *tina* itself, and having in its centre a socket (2½ inches across by 1½ inch deep) to receive the bearing of the upright shaft to which the scrubbers or agitators

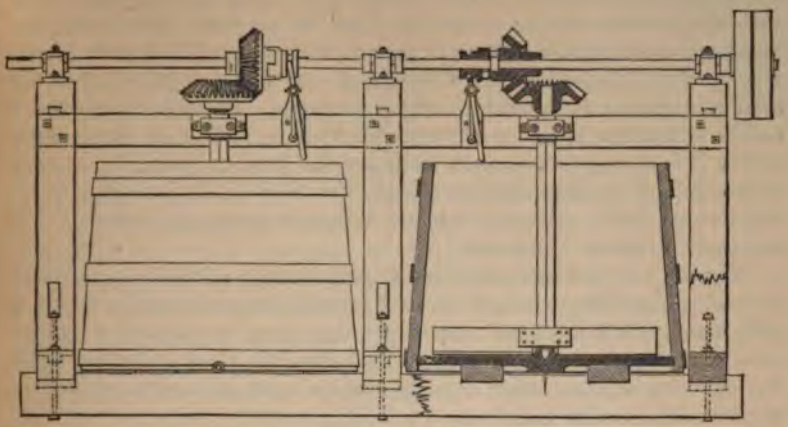

Fig. 86. Elevation and section.

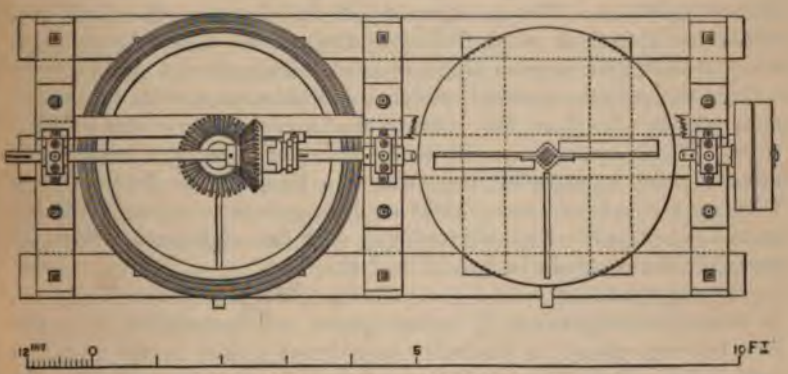

Fig. 87. Plan of the top and of the bottom plate.

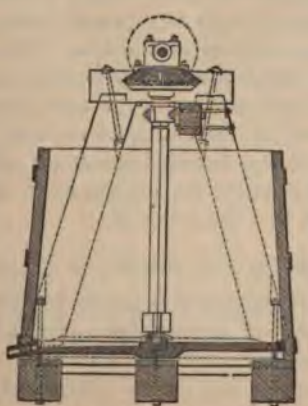

Fig. 88. Vertical section at right angles to that in fig. 86.

are attached, and also a radial groove or channel (1 inch wide by 1¼ inch deep), commencing at about three inches from the centre and terminating in a round tube or spout (with an orifice 1 inch in diameter), which projects some few inches outside the woodwork of the *tina*, and serves for drawing off its contents. The thickness of this cast-iron bottom plate is throughout 1½ inch, except in those parts where it is strengthened, such as under the socket, where, for a circle of six inches in diameter, it is cast 3 inches thick, and also under the groove, for a width of about 3 inches along its course, it is increased to about 2¼ inches.

Exactly in the centre, and on the under-side of the bottom plate, a small round hole or socket, about ⅝ inch in diameter and in depth, is left, which fits down upon a corresponding plug or spike of wrought-iron, driven into the framework: this, when the *tinas* are being fitted up, or when replaced after repairs, enables them to be at once centred or placed in correct position.

The *tinas* stand upon cross planks resting on a framework which supports the shaft and gearing used for giving motion to the scrubbers or agitators. The arrangement of this framework, which may either be of iron or wood, differs in the various establishments; in some of these, six or even eight *tinas* are arranged in a circle around a large central crown-wheel, which communicates motion to smaller spur-wheels, placed on the vertical shafts pertaining to the different *tinas*. Where space, however, is not of importance, it is found more advantageous to place all the *tinas* in a line, and to drive each of them by a couple of bevel-wheels so arranged as to be easily thrown in and out of gear without interfering with its neighbours. Such an arrangement is shown in figs. 86 and 87.

The upright shaft which gives motion to the scrubbers or agitators, is made of wrought-iron 2½ inches square, and rests below in a cast-iron bearing, placed in the before-mentioned socket in the cast-iron bottom plate, whilst above it works in bearings attached to the framework.

The scrubbers or agitators have two or three arms fixed on to the vertical shaft, sufficiently high to rotate at about from ¼ to ½ an inch at most above the iron bottom of the *tina*. They are made either of wrought- or cast-iron, and sometimes formed by merely attaching a piece of flat bar-iron with screws to the upright shaft, but it is better to have the lower half of each arm of such a bar bent in opposite directions, as shown in the annexed woodcut; more usually, however, cast-iron arms of a triangular section are used, the arms being curved in opposite directions like the letter S.

DESCRIPTION OF THE PROCESS OF AMALGAMATION.

The process of amalgamation is conducted as follows:—The lower orifice or spout of the *tina* having been closed with a wooden plug, and the machinery set in motion, the *tina* is filled to about two-thirds of its capacity with water and ground silver ore; the quantity of ore for one charge usually varies from 4 to 6 cwt., but is dependent

mainly on the more or less muddy or tenacious character of the mixture of ore and water: mercury is then added. When the ores are poor, about 150 lbs. will be required to the charge, but more must be added in proportion as the ore is richer in silver, since if a sufficient excess of mercury be not present to keep the amalgam fluid, it is apt to become hard and set upon the bottom of the *tina*, so fast as even to risk a breakage of the machinery.

The scrubbers are kept in constant motion (ordinarily a speed of about 16 revolutions per minute is found sufficient) until the amalgamation of the charge has been effected; from time to time the state of the amalgam is examined, by working a little of the mercury in a small round dish or saucer made of black unglazed earthenware (about 4½ inches in diameter and ½ inch in depth), which is locally called a "chua," a term probably of Indian origin.

The time occupied in completing a charge varies greatly, according to the nature of the ores under treatment. When the ores only contain native silver, from 4 to 6 hours is generally found sufficient; the chlorides and chlorobromides, however, require much more time, even up to 24 hours, on an average probably 20 hours. This appears to be chiefly owing to the difficulty of keeping the chloride of silver in these ores in contact with the mercury, particularly as during the operation of grinding, the horn-silver becomes flattened out into small scales which have a great tendency to keep suspended in the water of the *tinas*.

When the amalgamation is completed, the mercury is drawn off through the spout into an iron pot, after which the whole contents of the *tina* are flushed out into settling tanks or slime pits, in which the solid matter is deposited and classified under two heads, the heavier and coarser part being called "relaves," and the lighter slimes designated "lamas."[7]

AFTER-TREATMENT OF THE AMALGAM AND OF THE SILVER EXTRACTED THEREFROM.

The mercury which is drawn off with the silver amalgam, which being specifically lighter floats upon its surface, is run into canvas bags and allowed to drain, after which it is placed in conical iron moulds, formed in halves, hinged together vertically, and which when in position are held together by means of hasps; a round bar of iron, about 1 inch in diameter, is then placed in the centre of the mould, and the amalgam is beaten down around it with a rammer until the mould is quite full of solid amalgam, and all superfluous mercury has

[7] In Copiapó the silver amalgamating works are seldom connected with the mines, but form a separate branch of industry; the silver ores being received from the miners and reduced at fixed rates. The "relaves" are returned to the miners, but the "lamas" remain the property of the amalgamating works. As the mines become deeper the "relaves" increase in richness, from containing more of those silver compounds which do not yield up their silver to direct amalgamation; of late years, therefore, they have been worked over again by other processes, and immense quantities have been smelted along with copper ores, thereby producing an argentiferous copper regulus which is exported to Europe.

been squeezed out of it. Upon opening the mould and withdrawing the iron bar, the amalgam presents itself as a cone having an orifice or tube through its length, which facilitates the escape of the mercury from its interior, when the amalgam is subsequently heated; sometimes the moulds are made of wood, hexagonal in shape, and formed of strong staves held together by iron hoops.

When the ores are of ordinary character, the amalgam in this state consists of about 5 parts by weight of mercury to 1 of silver; but when the ores contain much native silver in coarser grains or fragments, it may contain as little as 3 parts of mercury to 1 of silver, or even less, which is owing to the fragments of silver not being entirely permeated by the mercury, but only attacked on their external surfaces, and afterwards becoming incorporated, or, as it were, soldered into the general mass of amalgam.

The amalgam is now "retorted," the mercury which distils off, being condensed in water. This operation is conducted in various ways at the different silver works, but most commonly under cast-iron bells, such as were used in Freiberg, and will be described in the sequel. Occasionally these are so arranged that the amalgam, which rests upon a tripod, can be depressed or elevated during the operation by means of a screw and gearing, so that it may be examined to ascertain whether all the mercury has been expelled, without interfering with the action of the furnace.

The spongy or porous cones of silver left behind, after all the mercury has been evaporated,—which, from their shape, are called "piñas," meaning pine-apples in Spanish,—are in this state returned to the miners, who in their turn sell them to the bankers, by whom they are melted into bars for exportation. The piña silver, from the different ores, varies greatly in purity, being from 800 thousandths up to nearly 1000 thousandths fine. Some of the piñas from ores from the Manta de Peralta, a shallow mine at Chañarcillo, were absolutely fine silver, yet the average from the other mines of this district would not be above 920 thousandths. The miners, by experience, have arrived at the conclusion that the mines whose workings do not exceed 50 fathoms in depth from the surface, yield a pure, and those below that depth an impure, piña silver; the former producing "minerales calidos," the latter chiefly "minerales frios."

The bankers in Copiapó, before purchasing the piña silver, always heat the piñas to redness for some time in a small reverberatory furnace, in order to ensure the complete volatilization of any remaining mercury. Upon cooling they are reweighed, and are generally found to have suffered an appreciable loss.

After this heating they are now melted down in a small reverberatory furnace formed wholly of "adobe" (*i.e.* clay tempered with horse dung), lined with a little fire-clay; the bed of the furnace holds a charge of 500 lbs. of silver, which is usually cast into three large ingots.

Upon fusion, fumes of the oxides of antimony and arsenic are

given off, and frequently also considerable yellow smoke, which no doubt arises from the presence of sulphide of arsenic.

After complete fusion, the silver is cast into bars in open iron moulds.

The upper surface of the bars is often very black and dirty, and sometimes coloured green, probably from traces of arseniate of copper. When the silver contains gold, the last bar tapped or laded out is invariably found to be much richer in gold than the preceding ones. The loss sustained in this melting is estimated at something under half per cent.

The woodcuts illustrative of the foregoing description have been prepared from the actual working drawings of a set of amalgamators designed and erected by Mr. Forbes in 1868 at the Thunder Bay Silver Works, Lake Superior, Canada, where they were employed in amalgamating ores containing silver in the native state, with only traces of sulphide of silver, which is finely disseminated through a quartzose rock, with occasionally a little calcite or veinstone. On reference to the scale upon which these *tinas* are drawn, it will be seen that they are somewhat smaller than those generally used in Chile, but otherwise they are in all respects essentially the same in construction and mode of working.

[A description of the Tina process will be found in a paper by Domeyko in the Annales des Mines, 1841, 3rd ser., 20. pp. 469 et seq —J. P.]

Amalgamation of Ores of Native Silver in the State of Chihuahua, Mexico.[8]

In a paper by Mr. H. B. Cornwall, of the School of Mines of Columbia College, New York, published in 1873, it is stated that nowhere in Mexico does native silver occur so abundantly as at Batopilas, a town in Southern Chihuahua, and in the neighbouring country; and that an American company has been "in eminently successful operation there for several years." The silver-bearing veins occur in diorite, and the gangue is white crystalline calcite. The native silver is accompanied by "black sulphide of silver," proustite, arsenical iron, galena, and zinc-blende, all of which occur only in very small quantity. In the mine to which this description particularly refers, the ore is found in pockets, and is sorted into three classes of the following values per ton, respectively: the first, $2500 and upwards,—the second, $1000 to $2500,—and the third, under $1000, averaging perhaps $250.

The ore is crushed in a battery of three small stamps, weighing about 300 lbs. each, with a fall of 9″, and a capacity of 8 tons per 24 hours; and from the stamps it drops on a screen, with $\frac{5}{8}$-inch

[8] The Treatment of Ores of Native Silver in Chihuahua. Statistics of Mines and Mining in the States and Territories west of the Rocky Mountains; being the fourth Annual Report of Rossiter W. Raymond, United States Commissioner of Mining Statistics. Washington, 1873. pp. 434 et seq. Mr. Cornwall remained for a year at Batopilas.

slits, whereby the larger lumps of silver are separated and remain on the screen. These lumps are refined along with the "retort-silver," while the ore which has passed through the screen is amalgamated in an *arrastre*, a kind of grinding mill, a description of which will be found at page 589, under the head of Amalgamation by the Mexican or Patio process, and to which therefore the reader is referred. The *arrastre* is 9′ in diameter, and has only two grinding stones (*voladoras*), weighing each from 600 to 800 lbs. It is the use of the *arrastre* for effecting amalgamation that constitutes the special point of interest in this process; but the machinery for working the mill is also interesting from its peculiarity.

The *arrastre* is built on the top of a pile of masonry in a deep pit; and from the centre of the former rises a shaft, which revolves on a pivot in a plate raised a little above the bed. From the shaft horizontal arms project beyond the rim of the *arrastre*, and from these arms descend rods which support a horizontal water-wheel placed a few inches above the bottom of the pit. In the periphery of this wheel, at intervals of 6″, are inserted slightly concave rectangular floats, which are called in Spanish *cucharas* (spoons). A stream of water, from the height of 8′, descends very rapidly through a tapering shoot (written also chute), from 12′ to 15′ long, and impinges upon the floats, acting solely by its momentum. A water-wheel of this kind, 20′ in diameter, will drive the *arrastre* with its two *voladoras* as fast as four stout mules, and at the same time work the small battery of stamps above described. Although there is great loss of power in thus applying water, yet where there is a superabundance, as is the case at Batopilas, it is of no consequence.

Each *arrastre* is charged with about a ton of ore from the stamps, and sufficient water is poured in to give the proper degree of consistency to the mass. When there is too little water, the ore is raised up and pushed forward by the *voladoras* without being ground; and when there is too much, the ore packs beneath them. More water is supplied from time to time, as occasion may require; and after the grinding has continued for about 8 hours, sufficient mercury is added to amalgamate all the silver in the ore. Generally the *arrastre* is charged with a ton daily of the third-class ore, for which about 25 lbs. of mercury are needed; and after 3 days' run, or whenever the amalgamator thinks proper, rich ore is added, requiring proportionally more mercury, in order that a suitable quantity of amalgam may be accumulated in the *arrastre*, preparatory to "cleaning up." Some hours after adding the mercury, the amalgamator washes a portion of the charge in a horn spoon, with a view to ascertain whether the proper quantity of mercury is present.

Every morning, after the silver appears to be thoroughly amalgamated, a large excess of water is put into the *arrastre* and the grinding continued during from 4 to 6 hours. After leaving the contents of the *arrastre* at rest for a short time, the water is run off, which carries along with it all the finely-ground and desilverized ore; and the coarser grains which remain are reground together

with the next charge. The tailings thus procured are so poor that the most experienced men in the place are unwilling to pay $3 per ton for them, with a view of treating them by the Patio process. They contain nearly the whole of the galena, zinc-blende, and arsenical iron of the ore, a very little mercury and amalgam, and any proustite that may occur, with the exception of a trace that stays in the amalgam, either owing to its density or to native silver adhering to it. Most of the sulphide of silver, being less brittle and therefore not so easily reduced to powder, settles to the bottom of the *arrastre* and is taken out with the amalgam, in which it is plainly visible after washing. The tailings, after the rich silver ore has been added, and just before a "clean-up," being more valuable, are saved for concentration, or treatment by the Patio process.

When the rich tailings have been run off, the top layer of coarsely ground ore is removed with iron scrapers and reserved for the next charge, after which the amalgam is scraped up and carried in wooden bowls (*bateas*) to the washing tank. This amalgam seems, to the superficial observer, scarcely anything more than coarse sand and slime. It is washed in shallow wooden bowls, with the addition of about 10% of the mercury used in the *arrastre*, stirred, and rubbed constantly with the hand, whereby clean amalgam is obtained. The dirt thus separated, being rich, is reserved for concentration by washing on the plane-table. The clean amalgam is strained in canvas cloths, and this is the most tedious part of the process, as a very firm amalgam is required for the method of "retorting" practised at these works. It is asserted that it is not sufficient to strain the amalgam in large bags by merely twisting them with a stick, but that it is necessary to operate upon small balls of amalgam not exceeding from 2″ to 2½″ in diameter, and to squeeze and rub them in the canvas with the hands. "The coarseness of the silver, which is frequently present in *nails*, renders the separation of the quicksilver impracticable by any other means yet tried; from the very fine-grained amalgam obtained in the Patio process the quicksilver is much more easily expressed." The heating of the pressed amalgam is conducted in a very primitive manner, which I do not think it worth while to describe. It is stated that in this amalgamation process ¾ oz. of mercury is lost per mark of silver produced.

The silver or crude bullion obtained from the amalgam is refined in a small reverberatory furnace built of *adobes* (sun-dried bricks), wood being the fuel. The charge is 600 lbs., which is worked off in 4 hours. A little litharge and lead are added in order to remove the impurities, sulphur, arsenic, iron, etc., carbonate of soda and borax being also used as fluxes. The loss is 7% on the crude bullion, and consists, to some extent, of silver and mercury. The refined silver is cast into bars, which weigh about 70 lbs. each, and, on the average, are only 988 fine.

The slags from the refining furnace, with the concentrated tailings from the washing of the amalgam, and sometimes other secondary products, are smelted occasionally in a small blast-furnace

with the addition of galena, and the resulting lead is used in refining the crude bullion in the manner above stated.

MEXICAN OR PATIO PROCESS.[a]

Until the modern discoveries in California, Mexico had, from the time of its conquest by Spain, been the chief silver-producing country in the world; and by far the greater part of the silver which it has yielded has been extracted by the process in question. Notwithstanding recent improvements in the metallurgical treatment of silver ores, the Mexican process still holds its ground, and continues to be practised in substantially the same manner as when it was first introduced. The mines of Mexico mostly occur in mountainous districts, at a considerable distance from the coast, where water-power rarely exists, where the supply of vegetable fuel, the only kind to be had, is generally too scanty for smelting operations on a large scale, and where transport, which is mainly performed on the backs of mules, is very expensive. When, as in many cases, the mines are far from the amalgamation works, and the ores, which are only hand-picked, do not contain more on the average than about 0·153% or 0·184% of silver (50 or 60 ozs. per ton), transport is a large item of cost.

The silver produced in Mexico is chiefly derived from sulphuretted ores, but not all silver ores are suitable for Patio amalgamation, and some are practically irreducible by that process. Accordingly the method of treatment must vary with the nature of the ore, and the different methods in use in Mexico are the four following:—

I. Hot amalgamation or the Cazo process, suitable only for ores in which the silver exists wholly or nearly wholly in the metallic state, or in combination with chlorine, bromine, or iodine.

II. Patio process, suitable for ores in which the silver exists in the state of simple or complex sulphides, and not associated with

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[a] Much of this article on Mexican Amalgamation was submitted to the late Mr. J. P. Clemes, who had been engaged for several years as a mining engineer in Mexico. He favoured me (December, 1869) with various important notes upon it, which I have interpolated. Mr. Clemes died of fever in Mexico in December, 1876. Part of the article was also submitted to the late Mr. Buchan, who promised to add the details of the practice at the Real del Monte Works, of which he was the Director. But alas! only a few days after this promise was made to me at a personal interview, Mr. Buchan died very suddenly. I had the pleasure of knowing him during many years, and receiving from him much interesting information respecting the Mexican process; and I deeply regret that the readers of this volume should be deprived of the advantage of further contributions to the subject from him. The following treatise, entitled "De la Production des Métaux Précieux au Mexique, considérée dans ses rapports avec la Géologie, la Métallurgie et l'Economie Politique; par St. Clair Duport. Paris, 1843," is, as far as I can judge, one of the best on the subject; and in the following pages I shall avail myself largely of its contents. The author states that in 1836 he became proprietor of the Parting Establishment (*i.e.* for the separation of gold from silver), where auriferous ingots were treated for the Mint of the city of Mexico, and that he had resided there almost continually since 1826. An elaborate and valuable paper by M. Laur, on the Metallurgy of Silver in Mexico, appeared in the Annales des Mines in 1871, 6th ser. vol. 20. Other treatises and papers from which I have derived information will be mentioned in the sequel.

blende or galena in large quantity,[1] or with more than from 3% to 4% of copper-pyrites: they should also be quite or nearly free from haloid salts of silver.

III. Barrel process, suitable for ores similar to those described under II., when they do not contain more than 3% or 4% of galena, blende or copper-pyrites in large quantity, or certain pyritic ores said to be irreducible by the Patio process.

IV. Smelting process, suitable for any kind of silver ore containing blende, galena (especially when rich in antimony), or copper- or iron-pyrites, in large quantities.

There are also two other processes, which are comparatively unimportant in an economical point of view, and which are carried on only to a limited extent in exceptional cases; they are as follow:—

I. Direct amalgamation of ores containing native silver at Batopilas, Chihuahua, which has been previously described.

II. Scorification on a bath of molten lead, for ores rich in chlorobromide of silver, such as occur at La Blanca, Zacatecas; and for ores very rich in sulphuretted compounds of silver, and comparatively free from gangue.

Occasionally it happens that ores contain considerable quantities both of haloid salts and sulphuretted compounds of silver, and these are treated first by the Cazo process to reduce the former, and subsequently by the Patio process to reduce the latter; or else they are subjected to a particular modification of the Patio process itself. However, in such cases the choice of method will be determined less by considerations of suitability than of profit. Thus poor but abundant ores which would give a much larger yield of silver by the Barrel than by the Patio process, are, nevertheless, best treated by the latter, the increase in the yield of silver not making up for the extra cost of the former process.

For the Patio process the ores are hand-picked, reduced under stamps to the size of coarse gravel, and then ground with the addition of water to the state of fine mud. The stamps resemble those used at the tin-mines in Cornwall; and the apparatus for grinding, which is termed in Spanish *arrastre*, much resembles the mill in which flint is ground for potteries. Three substances are used in the Amalgamation or Patio process as usually conducted, namely, common salt or chloride of sodium, or earthy matter named salt-earth containing that chloride—*magistral*, which is pyritic copper ore, so roasted with access of air as to form as much sulphate of copper as possible,—and metallic mercury. The ground ore in the state of mud is first mixed with due proportions of common salt and *magistral*, the former being generally added first, and the mercury last. The mixing is usually effected by the treading of horses or mules; but in some of the larger works, mechanical contrivances, to be described further on, are used for the purpose. After a certain period, which varies according to

[1] The expression "large quantity" is vague and indefinite; but I have not been able to obtain more precise information on the subject.

circumstances, the mercury will be found to contain silver in notable quantity; and when as much of the silver has thus been amalgamated as experience has shown to be economically practicable, the ore-mud is mixed with water in vats, and agitated, by which means the argentiferous mercury or amalgam subsides and collects at the bottom. The overlying muddy liquid is tapped out, and the amalgam wiped clean and filtered, whereby a large quantity of liquid mercury escapes and solid amalgam remains in the filter. This solid amalgam is heated sufficiently to expel all the mercury, and the residual silver is melted and cast into ingots or bars. Such is an outline of the Mexican or Patio process. The operation takes place on large level floors, in the open air (except in a few localities where the climate is colder on account of higher elevation), and paved with flag-stones, or boarded and caulked, in order to prevent escape of mercury by percolation. These floors are contained within large walled enclosures or courtyards, which are termed *patios*, in Spanish; and, accordingly, that word is applied to designate the process itself. An amalgamation work is termed in Spanish *hacienda de beneficio*.

Duport in his volume published in 1843 estimated that 82% of the total silver yielded by Mexico was extracted by the Patio process, 8% by hot amalgamation or the Cazo process (to be described in the sequel), and 10% by smelting.

Mr. Phillips stated in 1846 that about $\frac{4}{5}$ths of the total silver produced in Mexico was extracted by means of the Patio process.[1] According to a statement of Laur, published in 1871, 71% of the total silver produced in Mexico was extracted by the Patio process, 16% by the Barrel process, 3% by the Cazo process, and 10% by smelting. In 1875, according to J. M. Contreras, the average annual production of silver amounted to $20,000,000, of which $\frac{4}{5}$ths was obtained by the Patio process.[2]

The consideration of the theory of the Patio process will succeed the description of the details of the manipulation, etc.

SILVER MINES OF MEXICO AND NATURE OF THE ORES.

The principal silver mines of Mexico occur to the N.W. of the city of Mexico, in the main mountain ridge called "Sierra Madre," which forms the continuation of the Rocky Mountains of the United States, and trends from S.E. to N.W. It is chiefly composed of Devonian slates and limestones, which are frequently intersected and interlaid by trachyte-porphyry and diorite, but seldom by syenite or granite. The trachyte-porphyry is usually of a reddish colour, and consists of a felsitic mass, containing crystals of the following minerals, namely, oligoclase, sometimes also of orthoclase, but rarely of glassy feldspar

[1] Descriptive Notice of the Silver Mines and Amalgamation Process of Mexico, by John Phillips, Esq., Secretary to the Real del Monte Mining Company. [Pamphlet, extracted from the Railway Register.] London, 1846, p. 20.

[2] Empleo de los ensayes de pella y de residuos para determinar los adelantes y fin de la amalgamacion de la plata en el beneficio de patio. By Manuel María Contreras. It is a pamphlet for which I am indebted to Don Mariano Bárcena, of the city of Mexico.

(sanidin), quartz, and partly decomposed hornblende. The diorite has a greenish colour, and is composed of an intimate mixture of oligoclase and hornblende, occasionally enclosing crystals of magnetite. Metamorphic rocks, such as hornblende-schist—serpentine—and sedimentary rocks of more recent formations, such as limestones and conglomerates, are occasionally met with. All the above-mentioned rocks are frequently intersected by dykes of basalt and trachyte of a more recent appearance. The silver deposits generally occur as lodes varying much in width, and bearing from E. to W., but in their western part often assuming a north-westerly direction. The dip of these lodes varies according to the line of elevation of the country-rock. Silver lodes occur in the sedimentary rocks, as well as in the trachyte-porphyry, which assumes then a stratified appearance; but a considerably larger amount of silver has been obtained from the former than from the latter group of rocks. Dioritic dykes occurring in the vicinity of silver lodes are said to indicate increased richness in silver.

In most of the silver lodes of Mexico the following three zones have been distinguished:—

I. The upper zone, named "quemazon," in which the matrix of the lode consists of a mixture of minerals, wherein manganese ores (psilomelan and pyrolusite) predominate.

II. The middle zone, named "colorado," characterised by the red colour of the matrix, due to intermixture of sesquioxide of iron.

III. The lower zone, named "pinto azul," in which the quartzose matrix is either of a grey or bluish colour, owing to the presence of various silver ores.

In the first two zones the silver chiefly occurs either native or as chloride and chloro-bromide, and in the last zone as sulphides, simple and complex.

The workings of the older mines are generally situated in the third or lower zone.

Nature of the Ores of the chief Mining Districts of Mexico.

Guanaxuato (this is the usual mode of spelling the word in English, but in Spanish it is Guanajuato).—The principal lode in this State is that designated *Veta Madre* (mother vein), which, according to Humboldt, usually varies in width from 49 to 59 feet,[4] but which in places reaches the extraordinary width of 60 metres, *i.e.* 197 feet, and which, before the discoveries in California, was regarded as the largest in the world. The gangue of this lode is chiefly a very white quartz, accompanied by amethyst, calcite, dolomite, and talc, rarely by fluor-spar, gypsum, spathic iron ore, apophyllite, asbestus, mountain-leather, and hyalitic quartz.[5] Silver is present as sulphide,

[4] Nouvelle Espagne. Paris, 1811. 2. pp. 525 et seq.

[5] Der Bergbau und das Amalgamations-Verfahren in dem Bergwerks-Districte von Guanajuato in Mexico, mit spezieller Beschreibung der Werke, welche das Haus der Señora Doña Francisca de P. Perez Galvez in demselben betreibt. Nach einem vom Königl. Preuss. Berg-Referendar, Herrn E. Tilmann, gearbeiteten Manuscripte. Münster, 1866, pp. 73.

as black—rarely red—antimonial sulphide, and in the state of metal. Crystals of native silver are very rare, but sulphide of silver in cubes is less so. The associated metalliferous minerals are iron- and copper-pyrites (the former almost always argentiferous[6]), galena, small quantities of brown blende, mispickel, and gold which is seldom visible. The ore contains scarcely 3% of its weight of metalliferous minerals, so-called, disseminated in the quartzose gangue. The *Veta Madre* is particularly distinguished from the lodes of Zacatecas, by its being wholly free from sulphate of baryta and chloride of silver. The average proportion of silver is estimated at from 0·15% to 0·2%, and rarely is ore found containing more than 0·3%. Under 0·09% the produce of silver does not (1843) pay the cost of mining and metallurgical treatment. The proportion of gold usually amounts to 0·5% of the weight of the silver. However, in different parts of the same concession or "take," notable variations have been observed with respect to the content of gold.[7] Mr. Clemes informed me that when he visited Guanaxuato in 1866 the bulk of the ores from the principal mines yielded only 6 marks of silver per *monton* of 3200 lbs., or scarcely 0·1%.

Zacatecas.—With respect to number and richness in silver, the mines in the State of Zacatecas come next to those of Guanaxuato. The principal lode is that designated *Veta Grande*, which occurs in the vicinity of the capital of the State. According to Burkart, it varies in width from 3 to 30 feet, and towards the east is usually divided into 3 or 4 branches, each from 1 to 20 feet wide. The silver occurs in the following states:—Native, chloride, argentite, an earthy variety of argentite termed by Burkart "Silberschwärze," stephanite, pyrargyrite, and very rarely proustite. The associated metalliferous minerals are galena, brown and black blende, stibnite, iron-pyrites, and very rarely copper-pyrites: the gangue is chiefly quartz, with hornstone, fragments of the containing rock, rarely calcite, and more rarely heavy spar.[8] The *colorados* (red ores) or gozzany parts, coloured by hydrous ferric oxide, usually extend to the depth of 80 metres, and contain native silver and "green silver" (*plata verde*, chloro-bromide of silver) in considerable quantity; but as the workings on the whole line have reached a much greater depth, that kind of ore forms only an insignificant proportion of the total raised. The *negros* or "black ores" (*i.e.* sulphuretted ores of silver) vary much in composition at different points of the lode. At some points quartz is mixed with a considerable quantity of pyrites, galena and blende; while at others, as at Gallega, the gangue is quartz, nearly as white as that of Guanaxuato, with disseminated red antimonial silver, often beautifully crystallized, and a little brown

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[6] Tilmann states that he had a specimen of this pyrites which was compact, somewhat pale in colour, and apparently pure, but which contained 24·56% of silver. He considered it to be a compound of sulphide of silver and iron in very variable proportions. See notice of the mineral, sternbergite, p. 200 antea.

[7] Duport, pp. 211 et seq.

[8] Aufenthalt und Reisen in Mexico in den Jahren 1825 bis 1834. Stuttgart, 136. 2. pp. 63 et seq.

blende, the metalliferous portion of the ore scarcely amounting to about 4% of the total raised. Between the depth of 250 and 300 metres, the *Veta Grande* has, like the principal lodes in Mexico, decreased in richness.[9] The greater part of the ore from the mines of San Clemente and San Nicolás is stated to be argentiferous pyrites, with native silver, the latter mine having yielded lumps of native silver weighing 25 lbs. each.[1] According to Humboldt, the silver extracted from the ore of Zacatecas does not contain gold, which he regards as a remarkable peculiarity.[2]

Fresnillo (a town in the State of Zacatecas).—The ores are, as elsewhere, divided into the two classes of *colorados* and *negros*. The *colorados* are described as yellowish and very friable, containing much hydrated sesquioxide of iron, metallic sulphides in small quantity, and silver occasionally in the state of bromide, but oftenest in that of metal. What is worthy of note is, that the change in the nature of the ore by weathering action is not in this locality confined to a certain depth; for even at the same level are found *colorados* and *negros*, thus showing that the component minerals have offered different degrees of resistance to the action of the same external causes of change; or, possibly, one part of the lode may from structural causes have offered greater obstruction to the percolation of water than another. In the *negros*, the gangue is quartz, in which are disseminated particles of blende, galena, especially iron-pyrites and arsenical pyrites, copper-pyrites in much less proportion, and silver chiefly in the states of simple and complex sulphides, but often also native, and chiefly in the capillary form. According to Burkart, the *negros* of Fresnillo usually consist of iron-pyrites, containing silver in the native state and as argentite, so finely disseminated that the particles of neither can be distinguished by the naked eye. He mentions besides a third kind of ore, *azulaques*, derived from the country-rock, which often for a distance of from 1 to 3 feet is impregnated with fine particles of iron-pyrites, argentite, chloride of silver, and native silver; the two latter also occur in thin plates in the fissures of the rock. The *azulaques* are often very rich in silver; and where they are extracted, the underground workings, usually very narrow, must obviously be made much wider.[3] In 1839 the average quantity of silver extracted was 6 marks $\frac{3}{4}$ oz. per *monton* of 20 quintals, *i.e.* about 0·15%; and if to this be added $\frac{1}{9}$ of this quantity as representing what is lost, the average actual content of silver in the ore may be estimated at 0·2%.[4] Burkhart states that in 1833 the average yield per *monton* of the *negros* was 10 marks, that of the *colorados* 7 marks, and that of the *azulaques* 6 marks.[5]

Guadalupe y Calvo (a town in the State of Zacatecas).—The ganguo is quartz, which is auriferous, particles of gold being often distinctly visible in the ore as extracted. Silver occurs chiefly as simple sul-

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[9] Duport, pp. 238 et seq.
[1] Phillips, Pamphlet, p. 5.
[2] Op. cit. 2. p. 507.
[3] Op. cit. 2. p. 89.
[4] Duport, pp. 257 et seq.
[5] Op. cit. 2. p. 89.

phide and seldom in the native state; red antimonial sulphide is very rare; and even in the region of the *colorados* or gozzan neither chloride nor chloro-bromide of silver is found. The associated minerals are iron-pyrites, and especially copper-pyrites, galena in small quantity, and blende in still smaller quantity. Towards the surface of the lode the gold and silver are pretty evenly disseminated in the quartz; but at a certain depth the reverse is the case, and those metals are concentrated in what are termed *bolas*, which are more or less rounded masses of great richness. The following results are given as to the produce of silver and gold from these ores:[6]—

	Silver.	Gold.
	Per cent.	Per cent.
Bolas	2·30	0·39
Considerable portion of the ore	1·30	0·10
Mass of the ore	0·39	0·02

Ramos (a town in the State of Zacatecas).—The gangue is a mixture of quartz, sulphate of lime, and clay coloured blue and green by carbonate of copper. Silver occurs as sulphide, red and black antimonial sulphide, and native. The *colorados* contain "green silver" or chloro-bromide in notable quantity. The associated minerals are highly argentiferous true grey (*fahlerz*) and purple copper ores. The ores of Ramos are stated to be remarkable for their richness in silver, and in that respect to be exceptional, the mines of Mexico being characterized by the abundance rather than the richness of the ores. In rich parts of the mine, named *Cocinera*, ore has been found which has been directly cupelled, in the same state as extracted, with twice its weight of lead, and yielded from 10 to 13 ozs. of silver per pound, when it was sulphide of silver; from 8 to 10 ozs. when it was red antimonial sulphide; and from 5 to 6 ozs. when it consisted of both of these species in admixture with true grey-copper ore. The ore destined for amalgamation is divided into three classes, containing the following porportions of silver:—

	Proportion of silver.		
	Per cent.		Per cent.
I.	8·33	to	10·00
II.	2·50	to	3·33
III.	1·33	to	1·66

The ore is often soft enough to render stamping unnecessary, and to admit of being sent direct to the *arrastres*.[7]

Sombrerete (a town in the State of Zacatecas).—The gangue is quartz, rarely exceeding 1 metre in width in the richest parts. Silver occurs chiefly as red antimonial sulphide, and the associated minerals are stated to be metallic sulphides, of which only iron-pyrites is mentioned. The proportion of such sulphides is so large, that these ores have always been regarded as little suited for the Patio process; and their relative richness in silver so considerable as to enable them to be smelted with advantage, which is the special

[6] Duport, op. cit. pp. 297 et seq.

[7] Ibid. pp. 343 et seq.

treatment at Sombrerete. The ores also from some mines contain so much galena as to render them specially suitable for smelting. The silver produced in this locality contains a little gold.[8]

Nieves (a small village in the State of Zacatecas, 15 leagues east of Sombrerete). — The ore consists of metallic sulphides, including galena, with quartz as gangue; and that from one highly plumbiferous lode contains 0·3% of silver. Only smelting is carried on, the fuel consisting of shrubs with which all the neighbouring hills are covered to a considerable distance.[9]

Angeles, La Blanca, Ojo Caliente (in the State of Zacatecas).—These localities are situated between the town of Zacatecas and the Peñon Blanco; and up to the period when St. Clair Duport published his treatise, they had only been the subjects of mining operations on a very small scale. The ore of Angeles, which is the principal locality, contains galena and an abundance of arsenical pyrites. The whole of the ore is washed on the *planilla* or concave buddle [*planilla* means in Spanish a small plane surface, and appears to be applied indiscriminately in Mexico to various kinds of dressing apparatus], and afterwards roasted in a *magistral* furnace, heated with palm-tree wood. During the latter operation sulphide of arsenic is evolved in immense quantity. The richest portion of the ore is smelted, and only the rest amalgamated.

The ores of the village of La Blanca, from the region of the *colorados*, are concentrated on the *planilla*. The resulting *schlich* contains much "green-silver" (chloro-bromide), and is treated by hot amalgamation or the Cazo process, to be described in the sequel; while the slime, in which "yellowish lead" (*plomb jaunâtre*, phosphate of lead?) predominates, is amalgamated in the Patio process. Burkart states that cerussite is also present in these ores.[1] It is generally maintained that native chloride of silver is not suitable for treatment in that process; but Lukner, who had had much experience in it in Mexico, assured Napier that the reverse is the fact, and that "horn-silver" can be reduced by it better than any other ore, provided the ore be ground extremely fine, and an excess of salt be added.[2] But Laur states that at La Blanca, when the ores contain a considerable quantity of argentite or chloro-bromide of silver, both of which are malleable in a certain degree, it is considered necessary, previous to amalgamation, to separate as far as practicable these two substances, and to treat them apart, in the manner described further on; their separation is effected by a washing and concentration of the pulverized ore. Pulverization is effected by stamps and subsequent grinding in *arrastres*, the resulting "slimes" are run into pits, and the "sand" deposited is concentrated on concave buddles (*planillas*). The "concentrations" rich in sulphide of silver are scorified on a bath of lead, and those rich in

[8] Duport, op. cit. pp. 347–352.
[9] Ibid. p. 351.
[1] Op. cit. 2. p. 167.
[2] The Mining and Smelting Magazine, 1. p. 309.

chloro-bromide, which usually consist chiefly of ferruginous sand, are treated by the Cazo process.

At Ojo Caliente, the ores pretty much resemble those of Guanaxuato, and are quartzose, containing galena and pyritic minerals in comparatively small proportion; *plata verde* and gold also occur: they were formerly chiefly treated by Patio amalgamation.

Real del Monte and Pachuca (neighbouring towns in the State of Mexico, the latter distant about 60 miles north-east of the city of Mexico).—There are numerous veins in this district, the most celebrated being the *Veta de la Viscayna*, from which Count de Regla from 1762 to 1781 derived more than £3,384,000.[3] The direction of this vein is from east to west, and its width varies from 13′ to 19′. The gangue is milky quartz, frequently passing into splintery hornstone, with amethyst, carbonate of lime, and a little sulphate of baryta; the silver exists as argentite, mixed with native silver, occasionally as stephanite and pyrargyrite; and the associated metalliferous minerals, so-called, are galena, blende in large quantity, true grey-copper ore (*fahlerz*), and iron- and copper-pyrites. Much of the ore raised in this district cannot be profitably treated by the Patio process, owing to the presence of too large a proportion of foreign sulphides, especially blende;[4] and of what is unsuitable for that process the richest is smelted in small blast-furnaces with the addition of lead-yielding substances, while the remainder is subjected to Barrel-amalgamation.[5] In 1853 the late Mr. Buchan, Director of the Real del Monte Company, informed me that the average content of silver in the ores treated by the Patio process (as determined by *dry* assay) was about 0·153%, or 50 ozs. per ton of 2240 lbs. Richter and Hübner stated in 1873 that the average yield of silver from *all* the ores varied, at that time, from 0·15% to 0·18% (*i.e.* from 49 to 59 ozs. per ton), and that the silver derived from the Patio process contained 0·2% of gold.

Zimapan (a town in the State of Mexico, to the north of Real del Monte).—The mines in the vicinity of this town supply lead-ores, which, according to Burkart, consist of galena, cerussite, and small quantities of native silver and argentite, associated with iron-pyrites, grey-copper ore, and arsenical pyrites; vanadiate of lead is also sometimes present (Duport); the gangue is formed of quartz, calcite, and fluor-spar.[6] These ores are smelted by the Real del Monte Company.

Zacualpan, *Sultepec*, *Tepantitlan* (three villages situated in the State of Mexico).—In the vicinity of the first two localities argentiferous lead-ores are found, which, in conjunction with the very rich cupriferous silver ores raised close to Tepantitlan, are smelted at the works De los Arcos.

Tasco (a town in the State of Mexico).—The gangue is milky

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[3] Humboldt, op. cit. 2. pp. 540 et seq.

[4] Laur, op. cit. p. 234.

[5] The Real del Monte Mining Company, Mexico. Report of the Director, John H. Buchan, Esq., March 1855. This is a very interesting and valuable Report, which is illustrated with three excellent plans and sections.

[6] Burkart, op. cit. 1. p. 294.

quartz mixed with carbonate of lime in large quantity. Silver occurs as red and black antimonial sulphide, and rarely native. The associated minerals are galena, white and magnetic iron-pyrites in abundance, blende in "truly surprising quantity," and rarely copper-pyrites. According to Humboldt, argentiferous antimonial grey-copper ore also occurs near Tasco. Transparent crystals of selenite, containing dendritic native silver, are found in the mines of Tasco; and their formation is ascribed to the action of the various decomposing metallic sulphides upon carbonate of lime, through the agency of percolating water. Infiltration of sulphate of lime may be observed upon the walls of the lodes, which traverse the limestone as well as the underlying schists.[7]

Catorce (a town in the State of San Luis Potosi).—The chief mines are in the region of the *colorados* or gozzan, which nowhere else has been worked to the same depth. The usual gangue is manganesiferous carbonate of lime. The principal ores of silver are "green silver" (*plata verde*), "ash-silver" (*plata ceniza*,—chloride of silver), and "blue silver" (*plata azul de Catorce*), which strongly effervesces on the addition of acids, and of which no accurate analysis had been given when St. Clair Duport's treatise was published in 1843. Thinly foliated native silver and sulphide of silver also occur, but less frequently. The associated minerals are carbonate and silicate of copper,[8] and sometimes, according to Humboldt, yellow and green lead ore (molybdate and phosphate of lead).[9]

Charcas (a town in the State of San Luis Potosi).—The ore is "black ore," *negro*, and consists of antimonial grey-copper ore, blende and galena, mixed with copper- and arsenical iron-pyrites; most of the silver appears to exist in the first two minerals above mentioned. The lode, *Santa Rosa*, consists of *negro* throughout its whole width. In another lode, *Minas Grandes*, the *negro* is found in large pockets in a confused mixture of carbonate of lime, greenish clays, and pyritic quartz. The average content of silver in the ore has varied from 0·15% to 0·25%; and there exist quantities of abandoned ore, containing 0·1% of silver. These blendiferous ores when treated by the amalgamation process, even after having been in some degree roasted, yield poor results, the mercury lost amounting to three times the weight of the silver extracted. Very numerous mine adventurers have been successively attracted to this district by the relative richness of the ores, but have been afterwards repelled by the difficulties attending the extraction of the silver. There are now only two mines of any importance, namely, the *Santa Rosa* and *Minas Grandes*.[1]

Sonora.—According to Mr. Clemes, another very important mining district is in the State of Sonora, Northern Mexico, where hundreds of mines are worked upon veins which occur chiefly in the spurs of the Sierra Madre and also high up in the main mountain-range. The

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[7] Duport, op. cit. pp. 336 et seq.
[8] Ibid. p. 287.
[9] Op. cit. 2. p. 507.
[1] Laur, op. cit. p. 206.

containing rock is generally porphyritic, but occasionally it is metamorphic limestone. The gangue is principally quartz and carbonate of lime, the latter sometimes in large proportion, and sulphate of baryta is also occasionally present. The prevailing ores are brittle silver (stephanite) and simple sulphide, with chloride and native silver rather rarely. The associated sulphides are iron- and copper-pyrites, blende and galena. In some of the veins the latter minerals are present in such quantity that the ores cannot be profitably treated by Patio amalgamation. The most important vein, both as to size and productiveness, which came under Mr. Clemes' notice in the northern district, is the *Veta Grande* of Promontorio near Alamos. Near the surface it attains a thickness of more than 50 feet, and consists largely of decomposed porphyritic matter; but the ores occur in a quartz gangue and are principally brittle silver and sulphides, with some argentiferous grey-copper ore (*fahlerz*) and copper-pyrites, which by decomposition give a green colour to the gangue. In one place, where a depth of 500 feet has been reached, the lode contains much galena and blende. The average yield of silver from these ores by the Patio process is 0·172% or 50 ozs. per ton of 2000 lbs.

Durango and Chihuahua (two States).—The State of Durango contains several important mining districts, and in the State of Chihuahua a number of lodes occur yielding an abundant supply of poor silver ores. In the famous mines of Batopilas, a town in the latter State, native silver has been found in large quantities; as much, it is stated by Ward, as 425 lbs. in one mass.[2] According to the same authority, the silver lodes of the district of "Jesus Maria," in the same State, contain a considerable quantity of gold near the surface, of which the quantity decreases, whilst that of the silver increases, in proportion to the depth. The great bulk of the ores, however, found in these States is very similar in character to those of Sonora.

Michoacan (part of the State of Valladolid).—The mines produce chiefly plumbiferous silver ores, most of which are smelted at works situated in the vicinity of the village of Troujes. In the district of the town of Angangueo there occurs one lode, named *Veta del Carmen*, which yields silver ores very rich in arsenic, and which, it is stated, require only a comparatively short time for their reduction by the Patio process.

Oaxaca (one of the southern States of Mexico).—Humboldt mentions an ore consisting of brown hæmatite, in which silver exists in the metallic state, disseminated in particles imperceptible to the naked eye; and that this "ochreous mixture" was the object of considerable operations at the mines of Angangueo, in what was then called the intendancy of Valladolid, as well as at Yxtepexi, in the province of Oaxaca. But the ore of the former locality contained

[2] Mexico, by H. G. Ward, Esq., His Majesty's Chargé d'Affaires in that Country during the years 1825, 1826, and part of 1827. London, 1829. vol. 2. p. 302.

argentite and stephanite, both undergoing decomposition, whilst only argentite is named as occurring in the latter, to which he ascribes the richness of the ore rather than to the metallic silver.[3]

Humboldt's General Remarks on the Silver Mines of Mexico.—At the beginning of this century Humboldt estimated that in the then kingdom of Mexico there were nearly 500 localities celebrated for the mines in their vicinity, and that probably there were about 3000 mines; and he adds, that it is not the richness of the ores, but their great abundance and the facility with which they can be raised, that distinguish the mines of America from those of Europe. "A traveller," he writes, "who visits the famous mine of Valenciana in Mexico, after having examined the *metalliferous* repositories of Clausthal, Freiberg, and Schemnitz, can scarcely conceive how a vein, which for a great part of its course contains the sulphide of silver disseminated in the lode in almost imperceptible particles, can regularly supply 230,000 ozs. per month, a quantity of silver equal to half of what is annually furnished by all the mines of Saxony."[4]

NOTES.—Since the article on Mexican amalgamation was in type I have great pleasure in announcing that my friend Mr. William James Newall, who has during the last eight years been engaged in conducting mining operations and amalgamation in Zacatecas, has visited London (April 1879) and rendered me most valuable assistance. He has read the whole of this article on Mexican amalgamation, corrected it in several particulars, and added much important information. I have interpolated many of his remarks in the text, but to have inserted all would have necessitated such extensive alterations in the type that I have felt myself compelled to introduce the greater part of them in the form of notes.

Colorados, p. 580.—Mr. Newall states that the *colorados* are, on an average, poorer in silver than the *negros*, and that few of them are now worked in the Zacatecas district; the proportion of silver which they contain is less constant than in the *negros*, but it is almost impossible to form an opinion respecting them by any examination other than an actual assay.

Veta Grande, p. 581, line 3.—At 420 varas in the principal shaft this lode is sterile.

San Clemente and San Nicolás, p. 581, line 5.—San Clemente and San Nicolás are on a system of lodes considerably to the south of *Veta Grande*, in fact nearly in the town of Zacatecas. The ores of this zone are the most refractory in the Zacatecas district, containing copper- and iron-pyrites, galena, and often blende and antimony. Malanoche, San Martin, and La Cantera mines also properly belong to this zone. Further south of Zacatecas is what may be called the third zone of the Zacatecas district, which, latterly, has been the

[3] Op. cit. 2. p. 508.

[4] The foregoing extracts are from Taylor's "Selections from the Works of Baron de Humboldt" relating to Mexico, London, 1824, and their accuracy has been verified by reference to the original.

most productive. Here the ores are more docile, the *colorados* being scarcely known, and the *negros* occurring almost at the surface. The silver exists as argentite and native, with fine-grained galena in small quantities, and gold; the gangue is chiefly composed of quartz and slate. Blende and ruby silver ore are rarely met with. Quebradilla, Bote, San Bartolo, San Rafael, and Carniceria are the principal mines on this zone.

Fresnillo, p. 581.—No mines are now (1879) worked in the Fresnillo district.

Ramos, p. 582.—No mines are now (1879) worked in the Ramos district.

DESCRIPTION OF THE PATIO PROCESS AS PRACTISED IN ZACATECAS AND ELSEWHERE IN MEXICO.

The late Mr. John H. Clement, mining engineer, who had been engaged during 18 years at Amalgamation Works in Zacatecas, communicated to me for publication (January 1857) a description of the process as practised in that district. I had the pleasure of numbering Mr. Clement, after his final departure from Mexico, amongst the members of the metallurgical class at the School of Mines; and for my instruction, during the period of his attendance, he conducted the process in miniature in my laboratory, operating upon ground ore which my friend, the late venerable Mr. John Taylor, had long previously obtained for me from the Real del Monte Works in Mexico. The experiment lasted during several weeks, and I had the satisfaction of observing in its course all the characteristic phenomena that have been recorded; and I doubt whether I should have learnt more from seeing tons treated instead of ounces. Mr. Clement's description, which is here presented *in extenso*, will be supplemented throughout with information derived from various sources.

Machinery for Stamping or Crushing.

Formerly stamps were universally used in Mexico; but of late years in some localities other methods of crushing have been adopted.

Molino (crushing-mill stamps).—In Zacatecas, the stamp-lifters are made of oak, and the stamp-heads of wrought-iron, both lifters and heads weighing 1 quintal (101·44 lbs.) each. There are 9 stamps to each mill, and each stamp falls 27 times per minute from a height of $22\frac{1}{2}''$. The stamp-heads last from 4 to 6 months, according to the quality of the metal. The crushed ore falls upon strong hides, which are perforated with numerous holes about $\frac{1}{2}''$ in diameter, and are kept stretched on a slope on each side of the stamps over a pit. These hides act the part of sieves, and allow only the ore when reduced to the proper size, when it is termed *granza*, to drop through into the pit

underneath.[5] A mill is worked by 3 mules driven abreast blindfolded, much as they are driven in the Cornish whims, the driver sitting on the end of the lever. The diameter of the mule-walk is 26′, and there are 4 turns per minute. The time of daily work is 14 hours, 2 hours out of the 14 being consumed in changing the mules. There are 18 mules to each mill, and 5 removes during the day. At each mill 1 man and 3 boys are employed. The work done is 6 tons of 2000 lbs. Spanish (1 ton = 20 quintals = 2028·8 lbs. avoirdupois) in 12 hours. Each mule is worth about $30 (about 7*l.*), and costs in keep per week 10 reals (5*s.* 5*d.*). It is stated that the men who work at the stamps are never allowed to go beyond the walls of the hacienda on any account, except on feast days, or Saturdays at night, and they resume work at 4 A.M. on Monday. They are all strictly searched before passing the outer doors. Such a search would also appear to be necessary in the case of the miners, as may be inferred from the following anecdote which was communicated to the Author by the late Captain Tindal. When that gentleman was manager of the Real del Monte Works, a dead mule was drawn up one of the shafts, which, it was pretended, had accidentally fallen to the bottom. It was, however, suspected that the poor animal had met with foul play, and on examining its body it was found that a considerable quantity of very rich ore had been concealed within it.

Bárcena informed me in 1875 that edge-stone mills had been substituted in Zacatecas for stamps, in the first crushing of the ore: the runners are made of porphyry, which abounds in the vicinity.

At Fresnillo, crushing-rolls, driven by steam-power, have been substituted for stamps. Each train of rolls consists of two pairs, one set over the other. The dimensions of the rolls are as follow:—Length 18″ (0·46 metre); diameter of the upper rolls 22½″ (0·57 metre), and that of the lower rolls 27⅛″ (0·69 metre). The rolls revolve about 9 times per minute, and two trains of rolls are capable of crushing 46,248 tons (47,000 metrical tons,—1 ton = 1000 kilogrammes) of ore per year.[6]

The stamping-mills for producing the "granza," even in the best arranged haciendas in Mexico, were (in 1866) very ineffective and wasteful of power. In the Sierra Madre of Sonora Blake's stone-breakers are employed for this purpose, and doubtless with great advantage, especially where steam- or water-power can be had. (Clemes.) There are, however, but few mining localities in Mexico where water-power is available.

Arrastre (from the Spanish verb *arrastrar*, to drag) or *Tahona* (grinding-mill).—It consists of a shallow flat-bottomed pit of hard material, in the centre of which revolves a vertical shaft, carrying four arms at right angles to it, to each of which is attached a heavy

[5] Journal of a Residence and Tour in the Republic of Mexico in the year 1826, with some Account of the Mines of that Country. By Captain G. F. Lyon, R.N., F.R.S. 2 vols. 12mo. 1828. See Notes at the end of the 2nd vol. on Amalgamation at the Hacienda of La Sauceda, Veta Grande, Zacatecas, pp. 275 et seq.

[6] Laur, op. cit. p. 121.

stone. The stones are fastened by thongs of bullock-hide, two hooks being inserted in the upper part of each stone for that purpose, as shown in the annexed woodcut, fig. 89. When the shaft revolves the stones are dragged round, and so exert a grinding action. Motion is communicated by mules or horses, and when available by water-power. In the latter case the upper part of the vertical shaft is fitted with a cog-wheel geared into a larger cog-wheel in communication with the water-wheel. In Zacatecas the *arrastre* is 9′ in diameter and 1′ in depth, and the bottom is formed of 13 stones, generally old *valadoras* (grinding-stones), or flat unhewn slabs of porphyry. Duport describes this porphyry as having hornstone for its base, and containing mammillated hyalite in considerable quantity in all its pores; and adds that it is used in *arrastres* on account of its

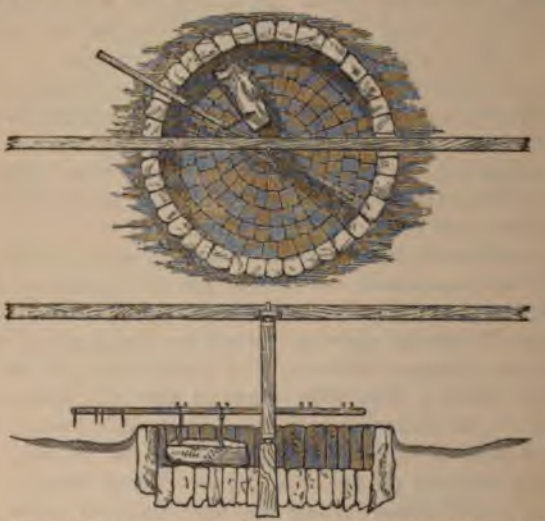

Fig. 89. Arrastre, shown in plan and vertical section, from drawings presented to me by the late Mr. Clemes.

Scale of 10 feet to 1 inch. Only two arms are shown, of which one is prolonged at the outer end beyond the border of the pit in order to allow of the attachment of mules to it.

hardness.[7] There are 4 stones for grinding (*voladoras*), of the following weights and dimensions:—

	Weights in lbs.	Length in inches.	Square in section. Width and height.
2 Grinders	1100 (each)	44	16½″
1 Mixer	600	24	—
1 Smoother	450	12 to 18.....	—

The two latter stones are fixed to the arm at right angles to that to which the mules are attached, and are the lightest in weight, the new stones being always put on the mule arm. The length of these stones should be the same as that of the grinders. In many *haciendas* stones of different grain are used; and workmen say that the coarse-

[7] Op. cit. p. 239.

grained stone grinds, whilst the close-grained one smoothes or mixes. (Newall.)

They last about 6 weeks, and cost $2 each (8*s.* 4*d.*). There are from 3½ to 4 turns per minute, with 2 mules driven abreast. Water is added from time to time as occasion may require. In 15 hours (Mr. Newall states 24) are ground 10 quintals (=1000 lbs. Spanish=1014·40 lbs. a.v.d.), of which time 3 hours are consumed in removing the mules, which are changed every 3 hours, and in discharging and loading. One man attends 3 *arrastres*, and receives 2 reals each per day (total 13*d.*); but this is not paid unless ore is delivered properly ground in due time. Mr. Newall states that they are generally paid by the job, from 4 to 5 reals per *monton* of 2000 lbs. Spanish. The first cost of an *arrastre* is about $56 (say 11*l.*). The timber-work lasts for centuries, and the stone bottoms last from 2 to 3 months with care. Duport states that the weight of the porphyry, removed in grinding, is estimated at from 6% to 10% of that of the ore.

In Guanaxuato, where the ore is ground much finer than in Zacatecas, only 6 quintals are passed through an *arrastre* in 24 hours.[8] The ore is softer and contains much clayey gangue; besides, fine-grinding is required for the extraction of the gold contained in the ore (Newall). In his treatise on Metallurgy, dated 1784, De Sarria states that "in the case of very rich ores the practice had been adopted of washing them on their leaving the *arrastre* in order to separate the more subtle portion called *lama* from the coarser called *cabecilla* and *polvillo*, the latter being either re-ground or treated on a bath of molten lead."

The late Mr. Buchan, when director and one of the proprietors of the Real del Monte Mining and Amalgamation establishment, informed me (October 1853) that 600 tons (1 ton=2240 lbs.) of ore were ground there every week. The *arrastres* were 11′ or 12′ in diameter, and he proposed to construct some 20′ in diameter. The bottom and the *voladoras* were made of basalt, which occurs in the vicinity of the works. According to Mr. Clemes, *arrastres* are now frequently 20′ in diameter. In Sonora and at Pachuca (Real del Monte) about 9 quintals are commonly ground in 24 hours in each *arrastre*.

The *arrastre* is almost universally used in Mexico for grinding ores, but the Californian stamping-mill, which is a most effective pulverizer, has been introduced in some places: its success however, in connection with the Patio process, has not been established. Clemes saw one at Guanaxuato, which was not favourably spoken of, and another at Alamos in Sonora, which was about to be supplemented with an *arrastre* driven by steam-power; and states that there was another in the same district in operation in 1869, the results of which he had not ascertained. Many others have been erected in connection with the Pan amalgamation process, and answer admirably; but the Patio

[8] Duport, op. cit. pp. 224, 225.

process requires a degree of fineness not readily obtainable by stamps, though wire-gauze screens as many as 6400 holes to the square inch have been tried.

At Fresnillo, *arrastres* 19′ (5·8 metres) in diameter and 1′ deep have been introduced; the total weight of the *voladoras* is nearly 6 tons (6000 kilogrammes); and the motive power is steam. With 16 such *arrastres* 34,249 tons (35,000 metrical tons) may be yearly treated. The use of steam is considered more economical than animal power, provided air-dried wood can be procured in sufficient quantity at 27·5 shillings per ton a.v.d. (34 francs per metrical ton. Laur).

Extraction of Gold.—In Guanaxuato, where the ores are auriferous, from 10 to 12 ozs. of mercury are put into each *arrastre* daily, in order to extract the gold. The mercury amalgamates with part of the silver and most of the gold in the ore, and the amalgam collects in the joints of the stones forming the bottom of the *arrastre*. The amalgam produced is very "dry," and is scraped out by means of an iron hook every 2 or 3 months. By distillation, this amalgam yields fine silver, containing from 4·5% to 6% of gold.[3] If the gold were left to be extracted by mercury in the Patio process, it would be associated with so large a quantity of silver as greatly to increase the cost of "parting." At one amalgamation work at Guanaxuato the following results were obtained. It was considered better to use mercury alloyed with a certain proportion of silver than the pure metal; and the reason assigned is, that pure mercury quickly finds its way to the bottom of the *arrastre*, and, there remaining in crevices between the stones, is to a great extent useless; whereas argentiferous amalgam becomes diffused over the bottom and so presents a large surface of action. The amalgam put into an *arrastre* was 70 lbs., and was composed of 56 lbs. of mercury and 14 lbs. of silver.

Pure mercury added subsequently at intervals during the grinding	330	lbs.
Mercury in the amalgam added	56	„
Silver and gold left (inclusive of the silver added in the amalgam) by volatilization of the mercury	84	„
	470	„
Weight of amalgam actually obtained	400	„
Loss	70	„

Assuming the gold extracted to have been present in the ore wholly in the metallic state, and deducting it (18 lbs.) from the residue (84 lbs.) obtained after driving off the mercury, there remain 66 lbs. of silver. This corresponds to a loss of nearly 1 part by weight of mercury for 1 of silver extracted, *i.e.* nearly equivalent proportions. Now the ores worked at Guanaxuato are stated to contain little or no native silver; and if this be so, it is obvious that a notable quantity of silver, namely (66 − 14 =) 52 lbs., had been directly reduced by

[3] Duport, op. cit. p. 224.

mercury, with the formation of sulphide of that metal. It is asserted that if, at the commencement of grinding, copper-amalgam, instead of silver-amalgam, be put into the *arrastres*, the copper will shortly disappear and the loss of mercury be somewhat lessened.[1]

The following more recent information on this subject has been published by Richter. For charges varying from 8 to 10 centners (1 ctr. = 50 kilogr. = 110·231 lbs. a.v.d.) the bottom of the *arrastre* is covered with a thin layer of copper-amalgam weighing from 8 to 10 lbs. According to the liquidity of the amalgam, from ½ to 2 lbs. of mercury are added every 3 or 4 days, the mercury being squeezed through a cloth so that it may fall in a finely-divided state. Generally after 2 months the *arrastre* is cleaned, when, on the average, from 18 to 20 lbs. of auriferous silver-amalgam, free from copper, are obtained. The yield of gold varies from 30% to 70% of that existing in the ore.[2] Gold in very fine particles seems to float away with the water, whilst some kinds of coarse-grained native gold resist amalgamation (Newall).

According to Laur, if the gold be not extracted in the *arrastre*, most of it will be found unamalgamated in the residues obtained in washing the *torta*.[3]

At Guadalupe y Calvo, also, mercury is introduced into the *arrastres* for the purpose of extracting gold and any silver which may be present in the metallic state.[4]

SUBSTANCES USED IN THE PATIO PROCESS.

The substances used in this process are, as previously stated, *magistral*, common salt or matters containing it, and mercury.

Magistral.

Magistral is usually produced by roasting copper-pyrites or other sulphuretted ores of copper, at a carefully regulated temperature, with free access of atmospheric air; and the essential agent contained in it is sulphate of protoxide of copper (cupric sulphate). When sulphide of iron is present, sulphate of protoxide of iron is at first formed, which as the temperature increases is successively resolved into sulphate of sesquioxide and sesquioxide, anhydrous sulphuric acid being disengaged. Sulphate of copper requires a notably higher temperature for its decomposition than sulphate either of protoxide or sesquioxide of iron; and, accordingly, in the preparation of *magistral* from copper-pyrites, the ore generally used for the purpose, the roasting is so regulated as to produce as much sulphate of copper as possible. If sulphuretted ores of copper should not be obtainable, *magistral* may be made by roasting oxidized ores of copper, such as red or black oxide, green or blue carbonate, or

[1] James Napier, jun., late Assayer at the Guanaxuato Mint. The Mining and Smelting Magazine, 1862. 1. p. 173.

[2] Die Bergwerke in Bezirke Pachuca und Real del Monte, und die Amalgamation in Guanaxuato, von Herrn Richter und Hübner. Preussische Zeitschrift, 1873. 21. pp. 110 et seq.

[3] Op. cit. p. 132.

[4] Duport, p. 313.

chrysocolla (hydrated silicate of protoxide of copper) in admixture with iron-pyrites; the sulphuric acid produced, as above explained, from the latter combining with the oxide of copper. In every case, previously to roasting for *magistral*, the ore is ground in the *arrastre*.[1] The notion is stated to exist, that the longer the pyritic copper ore is left exposed to the air before roasting, the greater will be the proportion of sulphate of copper yielded; but Napier asserts, that he has examined various samples of such ores which he had so exposed "for a length of time," without ever finding sulphates.[6]

The percentage of copper, iron, and sulphur of the ores used in the preparation of *magistral* in Zacatecas is shown in the following table:—

Kind of ore.	Locality.	Copper.	Iron.	Sulphur.
Yellow copper ore	Mazapil	20·00	8·46	14·24
Blue carbonate of copper*	Id.	28·00	3·14	8·86
Yellow copper ore	Tepezalá	6·00	17·22	20·78
Iron-pyrites (*marmajas*)[7]	La Sauceda[8]	—	26·50	25·50

* From the quantity of sulphur stated, the ore must have contained a considerable amount of pyritic ore.

At the Amalgamation Works named La Sauceda, three qualities of *magistral* are prepared from mixtures of ore and sea-salt from the Gulf of Colima. The proportions of the ingredients used for each quality and the percentage composition of the mixture are given in the following tabular statement, the qualities being indicated by the numbers I., II., and III. respectively.

PROPORTIONS OF INGREDIENTS.

	I.	II.	III.
	arrobas.	arrobas.	arrobas.
Yellow copper ore from Mazapil	..	..	9
Blue carbonate of copper from Mazapil	..	18	9
Yellow copper ore from Tepezalá	18	..	..
Iron-pyrites (*marmajas*) from La Sauceda	3	6	6
	almud.	almud.	almud.
Sea-salt from Colima	1½	1	1½

PERCENTAGE OF COPPER, IRON, SULPHUR, AND SALT IN THE MIXTURES.

	I.	II.	III.
Copper	5·30	21·00	18·00
Iron	18·56	8·98	10·97
Sulphur	21·46	13·02	15·03
Sea-salt from Colima	0·02	0·02	0·03
The *magistral* contained of salts soluble in water, per cent.	22	38	35
The quantities of these three qualities of *magistral* required for 1 ton (2000 lbs.) of the ordinary ore from the mine of La Gallega, containing from 64 to 80 ozs. of silver per ton (2000 lbs.), were	lbs. 45	lbs. 39	lbs. 37

1 arroba = 25 lbs.; 1 almud = 1·144 carga (measure) = 0·1292 bushel = about 30 lbs. of white salt of Colima. Mr. Newall informs me that Colima salt is now (1879) seldom if ever seen in Zacatecas, as the price is much higher than that of salt from other localities; and he thinks that the same may also be said of Guanaxuato.

[5] Duport, op. cit. p. 98.

[6] The Mining and Smelting Magazine, 1. p. 232.

[7] Pyritic residue or *schlich*, obtained in the process of separating the argentiferous amalgam by washing. See further on, p. 624. Duport, p. 250.

[8] The name of one of the Amalgamation-works in Zacatecas.

The foregoing determinations were made by Mr. G. Smith in 1837.

According to Laur, the copper ores used in the preparation of *magistral* contain from 3 to 16 ozs. of silver per ton.

Tepezalá is situated 49 miles (18 leagues, a Mexican league = 2·725 English miles: Ward's Mexico) from Zacatecas, and about 109 (40 leagues) from Guanaxuato, and supplies most of the ore consumed in the preparation of *magistral*; because this ore contains a larger proportion of copper-pyrites relatively to the gangue, than that from the other pretty numerous copper mines. The gangue of the Tepezalá ore consists of quartz and carbonate of lime, of which the lime would combine with some of the sulphuric acid generated during the process of roasting, and so be injurious; but not much of this carbonate is present.

The furnaces employed in the preparation of *magistral* are reverberatory. The ore is supplied through a hole in the roof, which during roasting is stopped up with a stone.[9]

In Guanaxuato the arch is very low, and the fire-place is in the middle of the bed, at each end of which is a chimney; or the furnace may be described as double-bedded. The usual charge of pyritic ore for each bed is 4 quintals (184 kilog. = 405·7 lbs. avoird.), and the operation is completed in 6 hours, with a consumption of wood as fuel not less than $1\frac{1}{2}$ times the weight of the ore, the furnace having been previously heated in the course of working. According to Napier, the ore is mixed with a few handfuls of common salt before it is put into the furnace. In Guanaxuato, according to Laur, *magistral* prepared in the following manner has, it is stated, been used with great advantage. Sulphuretted copper ore is first roasted nearly sweet, and then further roasted during an hour at low redness, with the addition of 16% of common salt intimately intermixed. By this treatment the copper is converted into chloride, but considerable loss, due to the volatilization of the chloride, occurs in the process.[1]

Magistral of average richness, made from Tepezalá ores at the Hacienda de Bernardez, Zacatecas, has been found by Laur to contain—

	Per cent.
Cupric sulphate (anhydrous)	9.03
Oxide of copper in the residue, insoluble in water	5·00
Ferrous sulphate	6·75
Ferric oxide	18·75

The other ingredients were not determined (op. cit. p. 76).

Berthier analysed *magistral* of first quality, which Duport obtained from Guanaxuato, and gave the composition as follows:[2]—

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[9] Duport, op. cit. pp. 92 et seq. This treatise, it should be remembered, was published so long ago as 1843.

[1] Op. cit. p. 77.

[2] Op. cit. p. 96.

	Per cent.
Cupric sulphate (anhydrous)	19·0
Ferrous sulphate	0·5
Sulphate of lime	2·5
Ferric oxide	25·0
Oxide of copper (CuO)	4·0
Sulphuric acid	0·8
Green stony gangue	43·2
Water	5·0
	100·0

Magistral of the first quality, at the Hacienda de San Juan, Guanaxuato, has been found by Laur to contain—

	Per cent.
Cupric sulphate	19·00
Oxide of copper	5·50
Ferrous sulphate	14·80
Ferric oxide	25·80

The quality of the *magistral* is tested as follows:—A small handful of it is kept squeezed in the closed fist, immersed in clean cold water, and the period, during which it may be held without relaxing the grasp from the heat developed, is noted. Should the sensation of burning become so intense before the lapse of half a minute as to necessitate opening the fist, it is designated *de piquete*, and is a kind that is not liked, because it occasions a larger loss of mercury than such as may be held in the closed fist during a minute or rather more. Mr. Newall, however, states that while some *azogueros* like *magistral* of this kind, others do not; but the general opinion is that the more the *magistral* burns the hand the better is its quality. In Lyon's work the following results are stated to have been observed at the Hacienda of La Sauceda, Zacatecas, concerning the temperature of *magistral*. The temperature in the air in the shade was 68° Fahr. at 7 A.M. and the day was gloomy. The temperature of a heap of dry *magistral* was 80° Fahr., and that of a handful of *magistral* wetted was 114° Fahr. The temperature of a heap of dry *marmaja* was 76° Fahr. and of a handful wetted 80° Fahr.

With regard to the old rule-of-thumb method of ascertaining the strength of *magistral*, Duport remarks, that the trial consisted in noting the degree of heat which it develops in the hand by the addition of a few drops of water. *Magistral* absorbs moisture from the atmosphere, the anhydrous sulphate of copper becoming hydrated, and in the course of 2 or 3 months after its preparation almost entirely loses this property, in which state it is declared to be no longer serviceable, and it is again roasted, but during a much shorter time. Now, when *magistral* is mixed with the ore-mud of the *torta*, the anhydrous sulphate of copper, which the former contains, must immediately or very soon afterwards become hydrated; and why, therefore, its efficacy should be impaired by previous slow atmospheric hydration is unintelligible, assuming, what may be demonstrated to be true, that sulphate of copper must be hydrated before

it can produce any effect in the amalgamation process. Indeed, according to Duport, the hydrated sulphate of copper produced in the operation of "parting" by sulphuric acid, had during several years, prior to 1843, been used with advantage in that process, and preferred "by all the enlightened *exploitants*, who, by its use, had got rid of the inevitable inconveniences arising from differences in the action of the *magistral*, of which the energy varies continually, either on account of the temperature in roasting, or the proportion of gangue in the ore, which latter cannot be made constant." Experience has shown that the application of 1 part by weight of the sulphate yielded about the same results as that of 5 parts by weight of *magistral* of the best quality, but in a shorter time, and seemingly with an increased yield of silver.[3] The sulphate is distributed in a finely-ground state over the mass.

In the larger works visited by Mr. Clemes in 1866, *magistral* was not used so generally as the crystallized sulphate of copper, which was preferred on account of its greater portability and uniformity of quality. In the cases that came under his observation the proportion added to the *lama*, containing, say, 60 ozs. of silver per ton of ore, was about 12 lbs. per ton of 2000 lbs. Mr. Newall says that Mr. Clemes must here have referred to Guanaxuato, as crystallized sulphate of copper is but little used in Zacatecas even at present (1879). He adds that in Guanaxuato the quality of *magistral* has always been better than in Zacatecas, because Tepezalá is further away from the former place, and the cost of transport does not allow the Tepezalá miners to send inferior kinds to Guanaxuato.

According to Laur, sulphate of copper is used at Pachuca and in Guanaxuato in the proportion of from 0·2 to 0·25 per 100 parts of ore,[4] *i.e.* from 4 to 5 lbs. per ton of 2000 lbs.

Ferric sulphate as magistral.—The comparative efficacy of this salt and cupric sulphate has been tested on a small scale in Guanaxuato in the following manner:—Two miniature *tortas*, containing each the same weight (2 kilog.) of the same kind of ore (containing 0·112% of silver), which was regarded as docile, were treated during 18 days at the same time with an equal weight of ferric and cupric sulphate respectively; the proportions of salt and mercury, and all other conditions, being the same in both cases. In the *torta*, with cupric sulphate—which *torta* served as guide—the loss of silver amounted to 15·8%, whereas with ferric sulphate it was not less than 65%.[5]

Salt (Chloride of Sodium).

Formerly the salt was obtained from sea-water by spontaneous evaporation; but, owing to the great cost of transit, whether from the Atlantic or Pacific coast, the saline deposit, or *saltierra*, which is left on the drying up of shallow inland lakes during summer, was, on account of its much less cost, substituted for common salt.

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[3] Duport, p. 227. [4] Op. cit. p. 145.
[5] Laur, op. cit. p. 263.

Formerly this *saltierra* was used in the same state as it was collected; but as it contains much inert matter (50% or more), the salt now chiefly used is prepared from *saltierra* and contains from 80% to 85% of chloride of sodium, the rest consisting chiefly of sulphate of soda. According to Mr. Newall, salt containing only 85% of chloride of sodium is not considered at all good, and at present (1879) the average percentage varies from 85 to 90, and sometimes reaches 95.

The salt lakes occur in the central plateau of Mexico, and salt from *saltierra* was first extracted from the Salina del Peñon Blanco, which is situated at the base of a granite rock on the plateau of Mexico, nearly midway between the cities of Zacatecas and San Luis Potosí. It is about 1½ mile wide and not less than 2 miles long. It is not unfrequently dry as early as at the end of January; and the bottom is formed of *saltierra*, which during many years has been scraped up for use in the Mexican amalgamation process. "The whole of this part of the country, to the distance of at least 45 or 60 miles, is composed of flattened hills and basins, of which the surface is covered with a bed of recent limestone, varying in thickness from 16½' or 20' to a thin crust of a few decimetres (1 decimetre = 3·94 inches), and pierced at different elevations with porphyritic igneous rocks. As in this district there is no ravine, which rapidly conducts the rain-water to the two seas (Atlantic and Pacific Oceans), and as both the porphyritic rocks and the beds of limestone are but little permeable, the rain which falls abundantly during 3 or 4 months forms a lake in the nearest basin. In the eight following dry months, the water in these temporary lakes is evaporated; and as it varies in composition, being very pure in some of them and charged with salts in others, saline deposits are left, consisting either of carbonate of soda (*tequesquite*), or a mixture of chloride of sodium and nitrate of potash, or of chloride of sodium mixed with a little sulphate of soda and some other insoluble salts, as in the lake of Peñon Blanco."[6] The *saltierra* of this lake was analysed at the École des Mines, in Paris, and found to have the following composition :—

Salts soluble in water ...	Chloride of sodium	19·0	21·2%
	Sulphate of soda	2·2	
Substances insoluble in water	Carbonate of lime	13·6	71·2%
	Carbonate of magnesia.....	1·6	
	Oxide of iron.....	9·8	
	Clay and sand.....	46·2	
Water and organic matter.....		7·6	7·6%
		100·0	

Since 1843 much white salt has been obtained by pumping the brine from wells sunk alongside the Salina del Peñon Blanco into tanks, and there leaving it to evaporate by sun-heat.

[6] Duport, p. 89.

This industry of extracting salt from *saltierra* has extended to other similar salt lakes on the plateau of Mexico, and now the establishments at Laguna Blanca, Chichimequillas, El Agrito, etc., supply Fresnillo, Zacatecas, and Durango with some salt; in the north, Alamos de Parras furnishes salt for a part of Chihuahua; and lastly the saline waters of the lake of Texcoco in the south are made use of by the Real del Monte companies.[7]

The following analyses of *saltierra* and of salt used in the amalgamation at Zacatecas and elsewhere were made by Spangenberg in 1836, and communicated to me by Mr. Clement:—

COMPOSITION PER CENT.

Locality.		Description.	Pure salt (NaCl.).	Carbonate of soda.	Sulphate of soda.	Earthy matter.	Carbonate of lime.
Lake-salt	Peñon Blanco 1st Class *	Salt-earth ...	44·80	4·00	3·20	42·00	6·00
		Id.	56·23	2·50	4·27	20·00	17·00
	Id. ..... 2nd Class †	Salt-earth ...	28·60	7·00	4·40	50·00	10·00
		Id.	28·00	6·25	3·25	56·50	6·00
		Id. commonly used.....	27·50	7·30	2·84	58·86	3·50
	Id.	White salt ..	93·21	2·29	2·00	1·50	1·00
	Del Moro	Id.	48·00	40·00	5·00	3·00	4·00
	Id.	Id. ‡.....	93·82	2·31	4·37	—	0·50
	Santa Clara ..	Id.	91·21	—	5·79	2·25	0·75
Sea-salt	Sal de la Mar (of the sea)	Id.	93·80	—	5·20	1·00	—
	Sal de San Blas	Id.	95·80	—	3·20	1·00	—

* Little of this is produced. † This is the chief class.

‡ There is probably an error of 1% in transcribing this analysis, but I do not know where to fix it.

The salt in these lakes is said to be mainly derived from a volcanic marl and clay formation, enclosing salt, gypsum, pumice-stone, and other volcanic products, and in a minor degree from hot saline springs.

Native carbonate of soda, *tequezquite*, occurs pretty abundantly on all the plains of the Mexican plateau, where, after the rainy season, it appears at the surface of the ground as a mealy efflorescence, which by the action of the winter frosts passes into a crust-like form. In the vicinity of the town of Fresnillo, in the State of Zacatecas, there are nine lakes yielding this salt, of which the principal one, named Salada, is situated a few leagues from Fresnillo, and has been formed in the same manner as that of Peñon Blanco. The salt is left by spontaneous evaporation of the water as a very dry whitish crust, covering the whole surface of the lake, which crust is collected in April, provided no rain has fallen in March, as is very rarely the case. The following analysis of *tequezquite* is by Berthier:[1]—

	Per cent.
Anhydrous carbonate of soda	51·6
Anhydrous sulphate of soda	15·3
Chloride of sodium.....	4·5
Water	24·6
Earthy matters	3·0
	99·0

[7] *Laur, op. cit. p. 64.* [1] Duport, p. 76.

Mercury.

Mercury is the only reagent needed in the Patio process that has to be imported from foreign countries. Although during the last three centuries cinnabar has been perseveringly sought for in Mexican territory, yet it has only been discovered in comparatively small quantity in a few localities,[2] of which the following may be mentioned:—near the village "El Doctor," situated at the foot of a mountain so called in the district of Zimapan (the name of the mine is San Onofre, the vein is about 9 feet wide, and in 1825 it is stated to have been worked with profit),[3] Rincon de Centerio near Guanaxuato, Durango, and Guadalcazar. Mr. Newall, however, informs me that, when in 1874–5 the price of mercury rose to more than $200 per quintal of 100 lbs. Spanish, many attempts were made to produce mercury in Mexico; and it was then found that the metal exists to a far greater extent than was supposed, and a considerable quantity was obtained by distillation in earthen pots. But the subsequent fall in price to $80 operated as a discouragement, and now (1879) only a few mercury works remain. Under the Spanish dominion the supply of mercury was derived from the mines of Almaden, in the south of Spain, which belonged to the Crown, and from Peru. Since the independence of Mexico the miners of this country have been free to purchase their mercury in the open market; but it was not until the discovery of rich mines of cinnabar in California in 1845 that they ceased to be dependent on the Almaden mines, which for many years have been leased to Messrs. Rothschild. It is fortunate for Mexico that this wealthy firm were unsuccessful in their attempts to purchase the Californian mines.

With reference to the injurious effect produced by restrictions upon the sale of mercury, the monopoly of which, as stated above, belonged to the Crown, Mr. Ward, formerly British Chargé d'Affaires in Mexico, makes the following statements:—"Although, by a series of judicious reductions, the price of this essential article was so much lowered as to place it within the reach of every class of Miners, still, the distribution of it (which depended upon the Viceroy) was by no means impartially regulated, the poorer Miners being generally sacrificed to the influence of the richer; while the necessity of concentrating the supply in one great depôt (the capital), and of effecting the importation through one solitary port (Vera Cruz), rendered the possibility of obtaining a sufficiency for the regular reduction of ores, in

[2] According to Laur, the only locality where cinnabar is now raised is that of Gaudalcazar, 28 leagues N.E. of San Luis Potosí; it occurs at Minas Viejas in nodules very irregularly diffused in limestone, which Laur considers to be of the same age as that of Catorce and San Pedro, namely Upper Jurassic, *i.e.* the Oolite of British geologists. Nearly 30 years ago the quantity of ore obtained amounted annually to 1000 quintals, *yielding* from 0·2% to 0·3% of mercury. In 1871 the mine was worked quite intermittently, and produced yearly less than 100 quintals of mercury. Op. cit. p. 71.

[3] Mexico. By H. G. Ward, Esq., His Majesty's Chargé d'Affaires in that Country during the years 1825, 1826, and part of 1827. 2nd ed. London, 2. p. 129. According to Domeyko, the ore is seleniferous, and consists of about 4 equivalents of sulphide of mercury to 1 of selenide. Tratado de Ensayes, 1876. p. 453.

the North, extremely uncertain, although the want of it entailed upon the Mining proprietor inevitable ruin." (Mexico, 1. p. 396.) Mr. Ward further remarks that "the supply seldom being equal to the demand, the Miners paid large sums for the privilege of being allowed to purchase it in preference to others" (p. 78).

METHOD OF AMALGAMATING THE ORE.

The Patio process is everywhere practised in essentially the same manner, so that an account of the mode of conducting it at one establishment will apply equally to all. The following description, as previously intimated, is from the pen of the late Mr. Clement, and is founded on his long personal experience at amalgamation works in Zacatecas.

In Zacatecas the ore consists of antimonial sulphide of silver [the particular mineral species not stated], iron-pyrites, zinc-blende, carbonate of lime and quartz, the metalliferous portion, usually so called, forming, say, 30% and the gangue 70%. The ore, which was treated in the manner to be described, consisted of the crude and roasted ores of the classes known as antimonial sulphides and argentiferous iron-pyrites (*bronces*).

The ore is stamped to the state of coarse gravel (*granza*), and then ground in *arrastres* with the addition of water to the consistence of thin mud, which is termed *lama*. The grinding charge for each *arrastre* is 10 quintals. The degree of fineness is ascertained by rubbing a little of the mud upon the lobe of the left ear between the fore-finger and thumb of the left hand. [Mr. Newall says he never saw or heard of this use of the lobe of the ear, and that rubbing between the thumb and forefinger is the only practice.] The ground ore is conveyed direct from the *arrastres* to the amalgamation floor in 18-gallon casks, each cask being slung on a pole and carried by two men.[4] The ore, which is in the state of thin mud, is left to thicken sufficiently by spontaneous evaporation to admit of being manipulated, say, like moist earth; and with that object it is poured from the casks into temporary tanks of the following simple construction. The millers form a space upon the paved amalgamation floor of from 25′ to 30′ square, by arranging pieces of timber, 5″ thick by 9″ deep, in the manner shown in the annexed woodcut, fig. 90. These pieces are kept in their places by large stones on the outside, etc., and within dry horse-dung is trodden down against the sides. After the requisite drying, the pieces of timber are removed, and the ore is worked into flat circular heaps *in situ*, each consisting, say, of 60 tons, or, as they are termed, *montones* (of 2000 lbs. Spanish each, or 2029 lbs. a.v.d.); but these heaps vary considerably in size at different works, in some

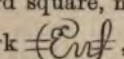
[4] The ground ore on leaving the *arrastre* is deposited, in an almost liquid state, in tanks of mason-work, named *cajetes* or *lameros* (Duport); and from these it is transferred to the temporary tanks described further on by Mr. Clement, and of which Duport gives a similar description.

works not containing more than 30 tons and in others only 8 tons. A *monton*, the unity of weight, varies considerably: in Guanaxuato it is 3200 lbs. Spanish (3246 lbs. a.v.d.); at Real del Monte 3000 lbs. (3043 lbs. a.v.d.); in Zacatecas, Catorce, and Fresnillo 2000 lbs. (2029 lbs. a.v.d.); and in some other districts it amounts to only 1800 lbs. (1826 lbs. a.v.d.).

The ore now passes out of the hands of the miller into those of the *azoguero*, or amalgamation-master. *Saltierra* or salt-earth,

Fig. 90. View of the Hacienda de Rocha, Guanaxuato, from photographs presented to me in 1876 by Don Mariano Bárcena, Secretary of the Mexican Natural History Society.

when of good quality, is added to the ore in the proportion of 18 *arrobas* (1 arroba = 25 lbs.), *i.e.* 450 lbs. per *monton* or ton of 2000 lbs., which corresponds to 128¼ lbs. of chloride of sodium per ton, or 6·4%. The salt-earth is well mixed with the ore, great care being taken to avoid superabundance of water, which, it is asserted, would necessitate the use of more magistral than otherwise would be required, and so increase the cost. In this operation of salting, which in Spanish is termed *ensalmorar*, 6 men and 12 horses a

employed.[5] After the addition and mixture of the salt-earth by the men, the heap of ore, termed *lamero*,[6] is made more or less circular, and then trodden by horses, which are guided by a long halter-rope held by a man and caused to walk in circles over every part of the heap: the circles so described are similar to those on an engine-turned watch-case. This operation of treading is termed *repaso*. The man who holds the rope must be constantly changing his position. After the lapse of an hour the horses are removed, and these 6 men, who have been engaged at intervals in shovelling in the rim of the heap of ore-mud or *lamero*, proceed, as much in line as possible, to turn over the heap with spades, just as a gardener would turn over soil, bringing what is at the bottom to the top. This operation, which is termed *traspaleo*, and lasts an hour with a 60-ton *lamero*, should be attentively watched by the captain, as lazy men will leave a coating of unmixed ore, *suadero*, on the flag-stones, and the results will be bad. The heap is again trodden by horses during an hour, after which it is made as round as possible by the 6 men, from 35′ to 40′ in diameter and 9″ in depth, and is left without any attempt at bordering. This done, a man, termed *tentadurero*, or "tryer," with the use of a wooden spade and a little water, makes a smooth place, about $\frac{1}{2}$ yard square, near the border of the heap, and impresses thereon the mark  , which means *ensalmoro*, or salted. This mode of marking the *torta* is, according to Mr. Newall, old-fashioned, and *azogueros* now (1879) seldom practise it. Thus ends the operation of salting; and woe betide the poor fellow who has left the heap sufficiently wet to enable the mark to be affixed without the use of water! The business of the *tentadurero* is to take samples for vanning by the captain and present the results to the amalgamation-master.

Mr. Newall informs me that he has found stallions to be the most serviceable for the treading of the *torta*.

On the following day, if all has gone on right, the next operation is proceeded with, which is termed the *incorporo*, or "incorporation," of the salted ore with the other reagents employed in the Mexican amalgamation process.[7] Immediately on entering the Patio at 6 A.M., the captain goes to the amalgamation-master to learn from him how much *magistral* and mercury is required. The ore under treatment contains, say, 8 marks or 64 ozs. of silver per *monton* or ton of 2000 lbs., that is, 480 marks or 240 lbs. (Spanish) of silver in the entire heap or *lamero* of 60 tons. This information is derived either from the previous working of the same class of ores on the large scale, or from

[5] Lyon states that a heap of *saltierra* is first piled in the centre of the provisional receptacle made of planks on the *patio* floor, and then the ore-mud or *lama* is poured in; and that when the last or sixtieth *monton* is introduced, the *saltierra* is shovelled down, and well mixed in by treading it with horses and turning it with shovels.—Op. cit. p. 7.

[6] According to Clement, the word *lamero* is also applied to the tank for receiving the ore-mud, as it leaves the *arrastre*.

[7] According to Duport, p. 106, the word *incorporo* is applied to the first dose of mercury added.

the amalgamation by way of experiment during several days of a *monton* or ton of the identical ore operated upon. It was not customary to assay the ore by any of the usual processes, dry or wet; and the proportion of silver, deduced in the manner above described, might be certainly estimated at 33% less than a correct assay would have indicated. [But at present (1879) Mr. Newall states that every mine and *hacienda* of any importance has its assayer and laboratory. There are also private assayers who charge 4 *reals* for each assay by scorification. In Guanaxuato crucible assaying is more general, because there larger buttons are required in order to determine the amount of gold by parting.] Let it be supposed that the amalgamation-master has found from his experiment upon a ton of ore that 39 lbs. of *magistral* will be required per ton, or a total of 7·86 loads of 300 lbs., for the entire heap, *i.e.* about 2%. But he has been taught by experience that proportionately less *magistral* is needed for a large mass of ore than for a small one; and he, accordingly, directs that 5 loads should be added to the heap or *lamero* of 60 tons in the first instance. The *magistral* is spread over the ore from wooden boxes, 18" long, 9" wide, and 9" deep, the heap being all the while trodden by horses at a gentle trot. This operation of "dusting in" the *magistral* lasts about half-an-hour and is carried on briskly, and the result is that the mass becomes spongy, dark-coloured, and warm to the men's feet up to their ankles. The men scrape the mud off their feet with a wooden knife. Twelve horses and as many men are employed in the incorporation process.

Immediately after the completion of the "dusting in" of the *magistral*, mercury is added, which is brought in small wooden barrels lined with white leather and laced externally with crude hide, each barrel being about 9" deep and 6" in diameter, and containing just 50 lbs. of the metal. Each barrel is carried by one man. [The common wrought-iron quicksilver bottle is now (1879) generally used.] A large square piece of brown linen is folded up into a bag by an expert workman, who places his left hand in the centre, and catching up the corners by his right hand turns them round his left wrist. Into this bag another man pours, say, from 6 to 10 lbs. of mercury, when the man holding the bag with both hands gives it a circular swinging movement, whereby the mercury is forced through the linen and spread over the heap of ore in the state of small globules. The heap or *lamero* now acquires the designation of *torta*, which means "cake" in Spanish. During from 1½ to 2 hours the horses are kept trotting over the heap, at a somewhat brisker pace than previously, and the men are engaged at other work until they are wanted to turn the heap over. By long practice, it has been established that there should be 6 marks or 3 lbs. of mercury to every mark of silver which it is computed will be extracted from the *torta*.[8] Consequently, 24 lbs. of mercury per ton or *monton* would be necessary, or a total of 1440 lbs. for a *torta* of

[8] This seems to be the general rule. The proportion of mercury used at Guanaxuato is the same. Duport, p. 107.

60 *montones;* but as each barrel holds exactly 50 lbs. of mercury, the amalgamation-master would prescribe 1450 lbs., or 29 barrels. Experience has shown that the whole of the mercury should not be added at once, but only $\frac{2}{3}$ in the first instance; and the order would, therefore, be given to add 20 barrels or 1000 lbs. in the *incorporo*.[9] [Mr. Newall informs me that now (1879) 3 lbs. of mercury per mark of silver is the quantity almost always put in at the *incorporo*, and no more is added until the *baño* or last portion.]

After an hour's treading or *repaso*, the *torta* is inspected, and for this purpose an average sample of the whole heap is obtained by a man skilled in this kind of work. He takes small portions of the ore-mud from every part of the heap, at the top as well as underneath. He walks in a serpentine course over the *torta*, and with the use of a wooden knife first collects the ore at the upper part of the heap; next he shoves one foot in a slanting direction along the stone floor, thus opening a space for the collection of ore from the lower part of the heap; and so he proceeds until he has got from 1 to 2 lbs. of ore.[1] This operation seems very simple, but it needs skill, and its performance in a slovenly manner may lead to serious error in judgment and consequent loss. The captain of the Patio receives the sample of ore-mud, and carefully washes it in a vanning horn (which is a bullock's horn cut longitudinally into two equal parts) or bowl, breaking up the mass with his fingers as delicately as possible, in order not to affect the character of the metalliferous product separated, including mercury, from the appearance of which product judgment is formed respecting the state of the process. After pouring off the muddy water, he clears away the bulk of the mass by careful vanning, keeping up a tremulous motion with the wrist. It is difficult to attain the necessary skill in this manipulation. Already, after the lapse of only 2 hours, some silver will be found to have passed into the mercury, and formed amalgam in a state of dust so fine as to be compared with the down on a moth's wing; which dust would be lost if the operation in question were unskilfully conducted. The residue or product of the vanning is handed by the captain of the Patio to the amalgamation-master, in order that he may examine it and instruct the former how further to proceed. [According to Mr. Newall, the mercury shows a marked physical change when, as yet, it contains no silver. This change is called *encadene* or "chaining," which will be further described in the sequel.]

[9] Napier gives the following indications of the proper degree of consistency of the ore-mud:—"The *torta*, when the mercury is added, should not be too wet, otherwise the mercury would be apt to collect into large globules again; neither should it be too dry, as the mercury in that case would become too much divided, and thus cause a larger loss than necessary in washing: it should be of such a consistency that the animals can, in treading, go through it with comparative ease, and yet leave the marks of their feet when removed."—Op. cit. *p.* 235.

[1] Duport states that the sample is taken from 20 or 30 points of the *torta*, that the quantity washed is about 8 ozs. (230 grammes), and that the washing is effected in an earthenware capsule, in the horn of an ox opened, or in a kind of calabash varnished, made out of the fruit of a tree. In my collection I have two such Mexican calabashes, which were presented to me by Mr. Clement. One is painted and varnished, and the other is in its natural state; both are prettily carved on the exterior.

In the metalliferous residue in the bowl, amounting to about ½ oz. in weight, there should be a mass of argentiferous mercury about as large as, and similar in form to, the upper third of an ounce leaden bullet divided horizontally into three pieces. By dexterous manipulation, the portion of the mass containing most mercury is thrown to one side divided into small globules, which remain aggregated and surrounded with a ring of silver-white powder. These globules are pressed pretty strongly between the thumb of the left hand and the sides of the bowl; the pressure is suddenly relaxed, and, if all has gone on well, silver-amalgam will adhere to the ball of the thumb, but will be quickly removed by putting the thumb gently on the large portion of mercury. When the foregoing indications occur, *magistral* to the amount of 1 or 2 additional *cargas* or loads of 300 lbs. is prescribed, the quantity being in a certain degree regulated according to the heat of the weather; but it is not added until after the *torta* has been turned over by men. In the months of March, April, May, and June, from about 8 A.M. to 2 P.M., the temperature ranged from 100° to 120° F. (*i.e.* 37·8° to 48·8° C.) in the sun, and from 60° to 80° F. (*i.e.* 15·5° to 26·7° C.) in the shade. The operation of turning over is effected in the manner previously described by 12 men, and lasts about an hour, after which a *tentadura* or trial of the ore is again made; and if indications like those observed on the first inspection are presented, then the mixing in of the additional *magistral* is proceeded with, say at 8½ A.M. By thus cautiously acting, care is taken to avoid adding *magistral* in excess, and to ensure that any portion of the ore which may not have received its proper share in the first instance shall now have that share.

The captain of the Patio should be present at the *incorporo*, during the turning over, and make the men keep the trench which they open in the ore 2′ wide at least; and this is specially necessary on account of the unevenness of the stone slabs forming the floor. Occasionally a pound or so of mercury will be found collected together on the floor, owing to the men, who added it, having been slow and careless in their movements while spreading it through the linen filter. This evil is cured by lifting a spadeful of ore-mud pretty high, and then with a quick turn letting it drop on the mercury. After the operation of turning over is ended, the horses, 12 in number, are made to travel carefully over the *torta* at a smart trot until about 11½ A.M., after which they are taken to two tanks and are well washed by their driver. Meanwhile, the other men are occupied in shovelling in the edge of the *torta* and making it as circular as possible, without any particular attempt at forming a border. These men are followed by sweepers who clean up round the *torta* after an *incorporo* without using water, care being taken not to wet the *torta*. The *tentadurero* and the captain, with a wooden spade just damped, make a smooth place of about half a yard square upon the surface of the *torta*, and impress thereon the sign (*i.e.* I. N. C. abbreviation of *incorporo*). This terminates the operations of the first day of the "incorporation." On carefully watching during a fine

warm afternoon, vapour may be observed escaping, and green chloride (oxychloride?) of copper formed round the escape-hole, in about 3 or 4 hours afterwards, say at 3 or 4 P.M.

On the following day the *torta* is left to rest (*reposar*). A careful amalgamator has assays made by vanning; but nothing is done, unless there is a very pressing demand for silver. On the 3rd day after the *incorporo*, at 6 A.M., the outer edge of the *torta* to the width of about 2′ is thrown inwards towards the centre, and the horses, now only 6 in number, are made to travel over the ore. If the mass has become hard, as is generally the case by this time, about six 18-gallon barrels of water are distributed over the *torta* with great care, and during an hour the horses are kept trotting over the ore; the whole mass is then turned over by 6 men with wooden spades, after which it is again subjected to the operation of trotting, whereby thorough intermixture of the ore and reagents is effected. The ore is again assayed, when it is generally found that there is no longer liquid mercury, but instead beautiful bright frosted dry amalgam, partly in mass, and partly in a very finely divided or dust-like state, forming an "eyebrow" (*ceja*) or crescent at the head of the vanning product. The term *limadura* or filings is commonly applied to the amalgam in this state, and properly so on account of its resemblance to silver filings. Should the "eyebrow" be slimy and tender to the touch, giving out minute globules of silver-coloured mercury, which run along leisurely, 1 or 2 more *cargas*, or loads of 300 lbs., of *magistral* must be added. On the contrary, should the entire "eyebrow" have become dry amalgam and hard, then is supplied the second portion of mercury, which is designated a *cebo*, which literally means food, and amounts to 9 barrels or 450 lbs., making the total mercury now added to be 1450 lbs. If, after the *torta* has again been turned over by the men, the "eyebrow" be still hard, 2 *cargas*, or loads of 300 lbs., of *magistral* may be applied, which will cause the mercury to become covered with a bluish-grey film and quicken the process of amalgamation. The *torta* is trodden by 6 horses until 11½ A.M., after which they are washed; the men round it off, forming a border 2′ wide all round the edge, and the *tentadurero*, with the captain, impresses upon it a mark indicating the day of the week when it was subjected to this treatment. Wednesday, *e.g.*, is thus represented (*miercoles*). This operation completes the 3rd day. On the 4th day the *torta* is left at rest, and on the 5th day it is examined and put through the same treatment as on the 3rd day; but neither mercury nor *magistral* is added unless the "eyebrow," seen after vanning, feels hard and rough when rubbed with the thumb, in which case a *carga*, or load of 300 lbs., of *magistral* is added. The 6th day, Sunday, is a *dies non*, and nothing is done. On the 7th day, Monday, the treading by 6 horses is repeated; but if the process is found to be going on sluggishly, 12 horses are employed, and after the subsequent turning over 1 or 2 *cargas* of *magistral* are supplied. It should be stated, that whenever a *torta* is subjected to a *repaso* or

Laur states that the amount of chloride of sodium added in the state of lake- or sea-salt varies at different works from 3·25% to 4·3%, according to the quantity of sulphides contained in the ores treated.

For the less sulphuretted ores of Guanaxuato the quantity of *magistral* added per *monton* of 3200 lbs. amounts to 18 lbs. on the average. As a general rule the quantity of *magistral* required varies, not with the amount of salt added to the *torta*, as Laur states, but, according to Mr. Newall, with the quality of the ore treated, salt always being used in excess, and, further, depends upon the season and the mean temperature. Contrary to what might be expected, Laur states that the same ores require during winter only half the quantity of *magistral* necessary during summer, and consequently ores containing a large proportion of metallic sulphides (*negros*), which require large additions of *magistral* for their treatment, are economically reserved for the winter season;[4] a custom of which, Mr. Newall states, he never heard. During the rainy season it is customary, according to Laur, to add twice the usual quantities of salt and *magistral;* but Mr. Newall informs me that there is no rule on this point, and that in Zacatecas he has never seen added at once more than 5 *arrobas* of *magistral* per *monton* at all seasons.

In Guanaxuato, where the ores are docile (*i.e.* easily amalgamated), the whole of the mercury required, which amounts there to from 3 to 3½ lbs., and in recent times even to 4 lbs. per mark of silver, is added at once in the beginning of the amalgamation. The last addition of mercury, however, "el baño," which is required in Zacatecas to render the dry amalgam sufficiently liquid, has been given up at all those works where from the beginning a sufficient quantity of mercury (8 for 1 of silver by weight) had been added to the *torta*.

The time required for the completion of the amalgamation process varies considerably. At Ramos and Fresnillo rich sulphuretted ores are amalgamated in from 8 to 12 days; whereas at the latter place a *torta*, composed wholly of *colorados* or gozzany ore rich in chloride and bromide of silver, requires sometimes 60 days until it has yielded its silver to the mercury. In Guanaxuato larger *tortas* require sometimes 40 days for the completion of the process. It may be generally stated, the higher the mean temperature of the locality the shorter is the period needed for amalgamation.

Mechanical Substitutes for treading by Mules or Horses.

In a few of the large establishments, instead of treading the *tortas* by animals, a simple mechanical contrivance, called in Sonora *alacran* (which means "scorpion" in Spanish), is provided, which is stated to be as effective and more economical, and which is shown in fig. 91. In the centre of the *torta* is a vertical post, which serves as a pivot for the end of a beam, which extends so far beyond the circumference as to admit of two mules being yoked to it, though

[4] Op. cit. p. 155.

only one mule is shown in the woodcut. Upon this beam rests another, to which is affixed a rack, that works into a small fixed

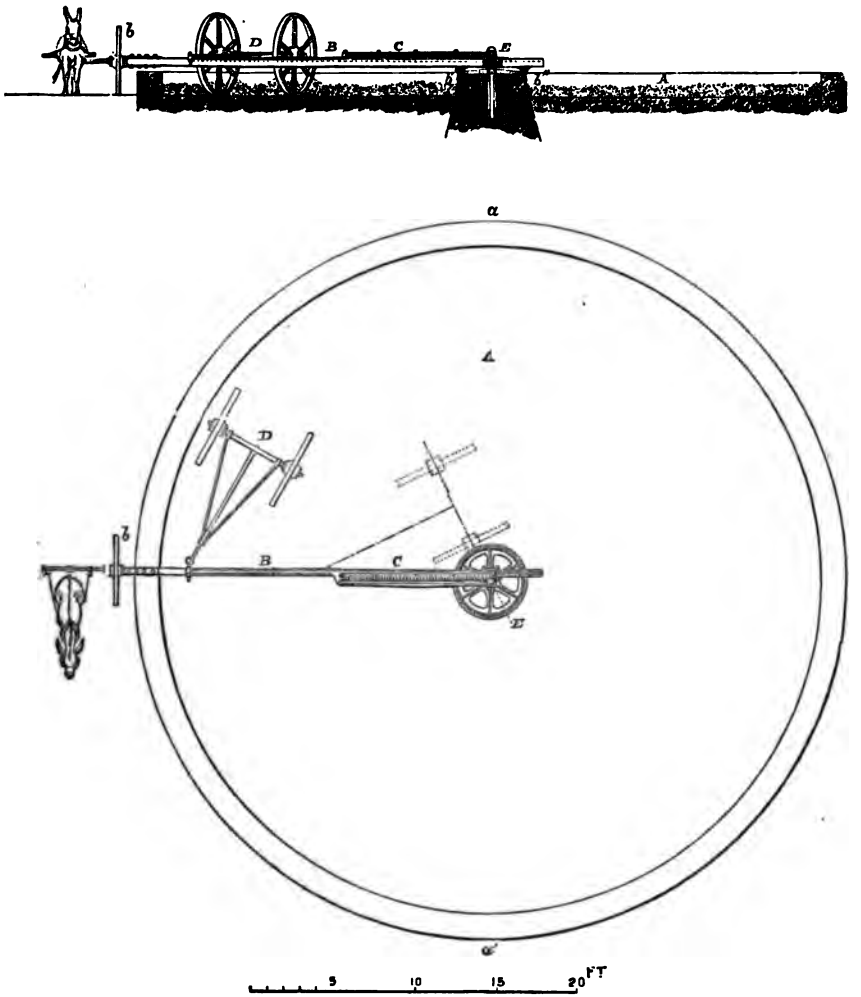


Fig. 91. Mechanical kneading, shown in vertical section through the centre, and in plan; from drawings supplied by the late Mr. J. P. Clemes.

A. The *torta*.
a, *a'*. Encircling wall of the *torta*.
B. Beam or shaft, grooved for receiving a sliding arm, the outer end having a spring-bar to which the mules are attached.
b, *b'*, *b''*. Tram-wheels for supporting the beam *B*.
C. Sliding beam or arm, with link and rack at the inner end and a hook attachment at the outer end.
D. Carriage attached to the outer end of the arm *C*, and consisting of a pole and axletree mounted on a pair of heavy wheels.
E. Toothed pinion fixed on the top of a vertical post in the centre of the *torta*, and geared into the rack of the sliding arm *C*.

toothed pinion in the top of the centre pivot. To this sliding beam is also attached one or two large heavy wheels, similar to cart-

wheels. As the mules are driven round the *torta*, these wheels knead the *lama*, and travel in a spiral course towards the centre; and by driving the mules in the opposite direction the operation is reversed. The turning of the heap is also sometimes effected with an apparatus similar to a plough, attached to the sliding beam in the place of wheels.

Mechanical Kneading at the Almada and Tirito Mines, Alamos, Sonora.

For the following description I am indebted to Mr. J. H. Clemes, formerly a student at the Royal School of Mines, London, and now engaged at the mines above mentioned. This ingenious contrivance was introduced about 1873 by Mr. Thomas Conant, a mechanical engineer at these mines. The machinery is represented in fig. 92, drawn by Mr. W. J. Prim from free-hand sketches.

The arrangement differs from the *alacran* in the following respects:—The beam to which the mules are attached is provided with a number of wheels, at equal intervals apart, for which it serves as an axis. These wheels, in revolving round the post in the centre of the *torta*, describe a series of epitrochoid curves which intersect each other at points continually varying. By this means, with a sufficient number of such wheels, every part of the *torta* in the course of time is kneaded. The path of one of the wheels is shown in the diagram in the lower part of fig. 92.

The new arrangement is said to be superior to the *alacran* in the following respects:—The mules or horses always travel in the same direction; with sufficient motive power more work can be done in the same time; and there is much less risk of breakage, a consideration of great importance in this part of Mexico, as the necessary repairs require the labour of a skilled mechanic, whose wages amount to not less than $150 per month.

This arrangement has been substituted for the *alacran* in several localities. However desirable it may be, especially in the case of "cold ores" (*metales frios*), to substitute mechanism for the treading by men or animals, it is doubtful whether any will be found equally effective.

One advantage resulting from the adoption of mechanical arrangements, such as those above described, is the prevention of suffering to the mules or horses, which, during the *repasos*, frequently

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a. Spur-wheel, attached by means of six rag-bolts to an upright stone block set in the centre of the *torta*.
a'. Pin, fixed in the centre of the spur-wheel.
b. Pinion, geared into the spur-wheel.
b'. Pin, fixed in the centre of the pinion.
c. Radius-arm, connected with, and revolving round, the centre of the spur-wheel, and carrying the pinion at its outer end.
c'. Guide-piece, bolted to the under-side of the radius-arm.
d. Socket, fitted for the reception of the pin *b'*, and hinged joint of the link.
d'. Connecting link, forming, with the socket, a hinged joint between the wheel, shaft, and the spur-gear.
e. Timber shaft, fitted with straps and a pin at the inner end for connecting with the link, and outer end, furnished with yoke or spring-bars for the attachment of the mules.
f. Wooden wheel, of which there are five, placed at equal intervals on and revolving round the shaft, *e*.

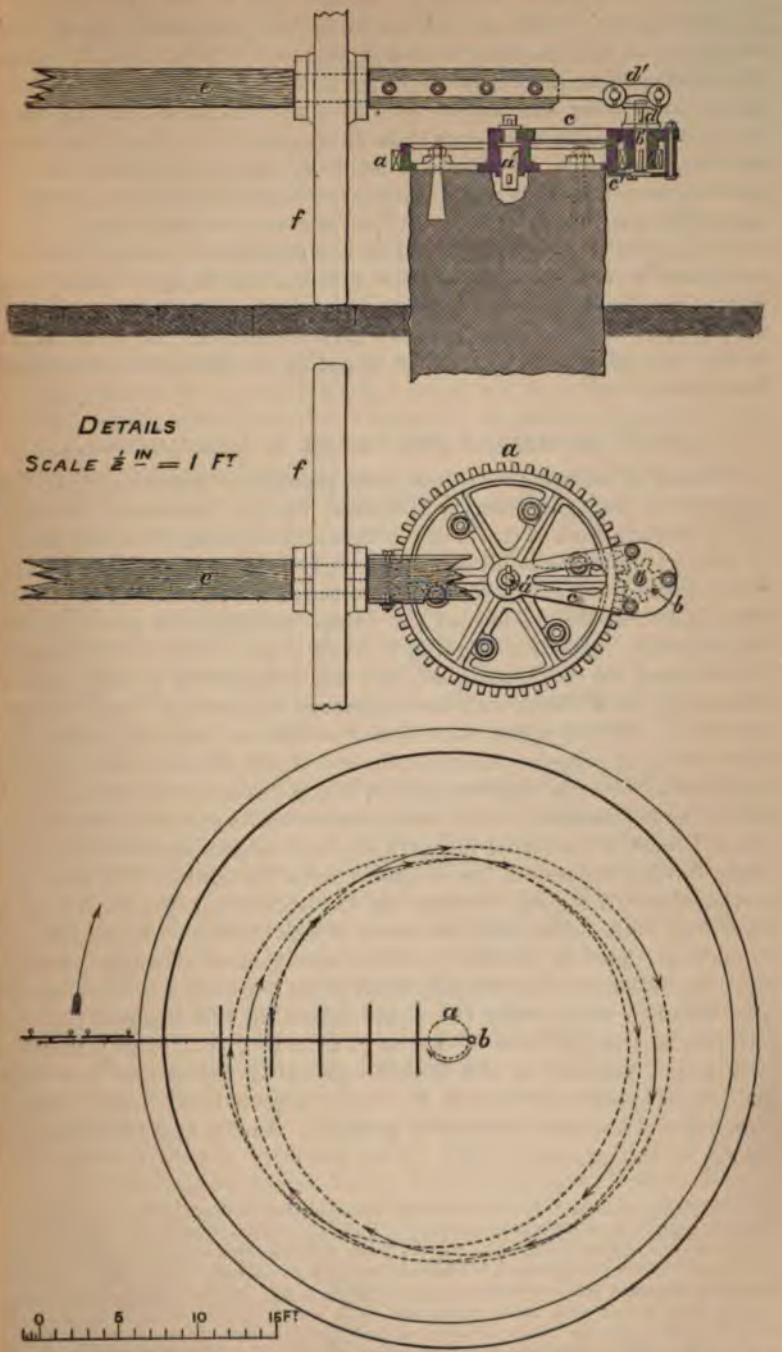

Fig. 92. Mechanical kneading apparatus in section and plan, with diagram showing the path of one wheel during four *revolutions* on the *torta* and three and a half revolutions of the pinion, being *equal to half the circumference* of the spur-wheel. [See description in the preceding page.

lick the ore-mud on account of the salt which it contains, in spite of every precaution that may be taken to hinder them from doing so. The consequence, according to Duport, is that occasionally they die prematurely from the action of the copper-salts, which moreover affect their legs, often causing them to ulcerate. Mr. Newall informs me that the hoofs are liable to drop off, especially in the case of pyritic ores; and that the treatment consists in the local application of human urine, or lemon-juice, substances which must differ much in their *modus operandi*. It is not uncommon to find a ball of amalgam in the stomach of the animals which have been long worked in the Patio process (Duport, p. 283); but it is stated that no injury is caused by contact with the mercury in the *torta*, either to the animals or men, even when kneading is effected by the latter barefooted.

SPECIAL REMARKS ON THE PROCESS OF AMALGAMATION.

Method of assaying.—It has been previously remarked that the progress of amalgamation is indicated by the *tentadura*[5] or assay which is made from portions of ore taken at intervals from the *torta*.

Duport gives the following description of the *tentadura* :—"In vanning the ore-mud (*i.e.* washing it in the manner described at p. 605) there is left at the bottom of the vessel metalliferous particles and the mercury. By then keeping a little clear water in the vessel, which must be held inclined, and communicating a very gentle movement, the different substances arrange themselves in the following order. At the upper edge is the portion of mercury which has been modified (*desecho*, thrown off) and finely-divided,—some little amalgam of silver in very fine grains, which has caused it to be named silver-filings (*limadura*),—the metalliferous *schlich* (*asiento*) comes next,—and lowest is the liquid mercury or the amalgam already solidified. After having separated the *limadura* from the *schlich*, the amalgamation-master rubs it, pressing his thumb against the bowl; and, according to its colour, and the more or less difficulty which he has in making it pass to the state of drier amalgam, of irregular shapes, termed *pasillas*, he forms his judgment of the beginning of the process. The *tentadura* taken after the *repaso* following the *incorporo* (*i.e.* the addition of the first dose of mercury, according to Duport), there is only liquid mercury at the bottom—provided the ore be not very rich in native silver—and at the upper edge a little finely-divided mercury and a commencement of *limadura*. In the first *tentadura* the colour of the mercury ought to be carefully observed. When it

[5] The term *tentadura* is also applied by Mexican miners to their mode of assaying specimens of ores of unknown character. In this case the specimen is ground very fine between two hard stones; the dust is then mixed with about an equal bulk of blasting powder, and the mixture is damped so much as to allow of its being moulded into an oblong lump; and the lump, being set on end on a stone, is lighted. After combustion has ceased, the residue is carefully collected and washed in a horn spoon and mercury added. By careful manipulation and skill, acquired by practice, a lump of amalgam is thus obtained, which affords by its size a fair idea of the value of the ore of silver. (J. P. Clemes.)

retains its natural colour, or its surface presents simply a bronzy tint, it is a sign that the process is going on slowly, and the *torta* is then said to have "got cold." When the surface of the mercury is a little grey, the process is going on well; but if the tint is dark, and the upper part of the *tentadura* presents an ash-grey powder, which cannot by friction be made to unite into globules, the process is going on too quickly, the mercury is too much attacked, and the *torta* is then said to be "heated." Supposing the proportion of *magistral* to be such that the operation proceeds properly, amalgam is found in the liquid mercury 24 hours after the *incorporo* (*i.e.* addition of first dose of mercury); on squeezing it, but little *desecho* is perceived at the other end where it has been replaced by larger and firmer (*plus consistante*) *limadura*, which, by friction, is changed into *pasillas*."[6]

Laur has given a very detailed account of the indications afforded by the *tentadura* in successive stages of the process, which in the main agrees with that of Duport. But he mentions the following additional indications, which seem to be interesting and important. The globule of mercury, 24 hours after the addition of mercury to the *torta*, has a decided pearly grey colour; and if a greyish cloud (*nuage grisâtre*) appears when it is rubbed under water, it should be slight; and when the globule is strongly compressed, it yields silver amalgam. Another statement made by Laur is that, so long as any silver remains unextracted, globules of mercury may be squeezed out of the *schlich*, adhesion between the two continuing only so long as it has not yielded up the whole of its silver. Laur also asserts that when amalgamation is completed the mercury resumes its natural colour. (Op. cit. pp. 146 et seq.)

Napier states that three *tentaduras* are made daily of each *torta*—one in the morning before the *repaso*, the second after the *repaso* has been going on for some time, and the third after its conclusion; and he adds that the process is always most advanced at the surface, where the ore-mud is most exposed to the action of the air and sun.[7]

Except in very anomalous cases, experienced amalgamation-masters will always be found to agree in opinion as to the indications afforded by the *tentadura* concerning the state of the *torta*; but they do not equally agree in opinion as to the period when the operation should terminate, and this leads to considerable differences in yield of silver. In a sort of competition between divers skilful amalgamation-masters in the treatment of the same ores, mixed and weighed with the greatest accuracy, the difference between the highest and lowest yields was 7%.[8]

Contreras points out (1875) the great advantage of being able to ascertain the degree to which amalgamation has progressed, and that this may be done by determining the proportions of silver in the little balls of amalgam (*pella*) successively obtained in the usual process of testing the state of the *torta*. As soon as that proportion

[6] Duport, p. 267.

[7] Op. cit. p. 345. Also Laur, op. cit. p. 141.

[8] Duport, p. 111.

becomes constant, after the whole of the mercury has been added, it may be inferred that the silver has been as completely extracted as possible.

Influence of the quality of the ore on amalgamation.—According to Laur, ores capable of being treated by the Patio process have always, with respect to the silver, a very simple composition; and such ores are designated by the Mexican miners *metales nobles* (noble ores). The following minerals, reducible by this process, are stated in the order of their reducibility, the first being most easily reducible: argentite, stephanite, polybasite, and certain varieties of argentiferous copper- and iron-pyrites not easy to define mineralogically, which are often very rich in silver, and undergo oxidation when impregnated with salt-water and left for a long time exposed to the air; on the contrary, argentiferous mispickel, proustite, chloride, bromide, and iodide of silver (*plata ceniza*, *plata verde*), argentiferous tennantite, bournonite, blende, galena, and other varieties of argentiferous iron- and copper-pyrites, are stated to be irreducible in the Patio process. Sonneschmid, on the contrary, asserts that hornsilver is the fittest ore for the Patio process, as indicated by theory and proved by experience! (Op. cit. p. 262.) Duport asserts that proustite is less easily reducible in the Patio process than pyrargyrite.[9]

Mr. Newall states that galena, and iron- and copper-pyrites, are not irreducible by the Patio process; and that, although they consume a good deal of sulphate of copper, they may yet be reduced with an active and careful *beneficio*, especially if copper be not too abundant in the pyrites. He has reduced ores of this description with a loss of not more than from 15% to 25% of the silver as determined by dry assay, and of from 14 to 18 ozs. of mercury per mark of silver.

When the ore contains only docile argentiferous species, the finer are the particles of the sulphides disseminated in the gangue, the more complete will be the reduction of the silver. This condition, which is always essential for a good yield, is particularly important, if the predominant argentiferous species is the simple sulphide (argentite). The malleability of this species is an obstacle to its complete trituration, as it laminates in the *arrastre* when it exists in the form of massive small nodules; and the resulting laminæ can only be attacked at the surface on the *patio*, whence considerable loss occurs. The *azogueros* moreover dread the presence of such nodules, and at well-managed mines they are either picked out by hand or separated by washing the crushed ore. (Laur, op. cit. pp. 99 et seq.)

In reference to the gangue and associated minerals, Laur makes the following observations:—Quartz and silicious minerals are the most favourable gangues for amalgamation; a clayey gangue produces mud of great plasticity, and causes subdivision of the mercury to the utmost extent, and in consequence considerable loss of

[9] Op. cit. p. 124.

that metal; dolomite is inert; whereas carbonate of lime, which is the exclusive gangue in some mines, decomposes the *magistral* and renders amalgamation very difficult. As ores which have been left to accumulate in the old workings contain acid salts, it is necessary to neutralize the latter with lime previously to amalgamation. Iron-pyrites in the ore permits the use of a comparatively large amount of *magistral*, and so of imparting great energy to the reactions from the first, without *heating* the *torta*. Copper-pyrites assists chemical action at first, and it is necessary to increase the proportion of *magistral* and frequently to turn over the mud; generally it is only attacked after some days' exposure in the *patio*, when immediately the *torta* heats and needs the instant addition of precipitated metallic copper. Blende is one of the most dangerous constituents of the ore, produces coldness in the *torta*, and necessitates an excess of *magistral*, which is almost immediately destroyed; the process is most irregular, and cannot be carried on without keeping the *torta* always hot. It is difficult to treat ore containing blende without losing from 175 to 180 parts of mercury to 100 of silver extracted; and if the blende is light brown (*blonde*) in colour and is very abundant, the ore becomes absolutely intractable in the *patio*, and the silver from blendiferous silver ores can be extracted only by working the *torta* hot;[1] but the loss of mercury amounts in such cases to from 175 to 180 per 100 of the silver extracted. Ores very rich in blende, such as those of Tasco, have to be roasted with the addition of from 1% to 2% of salt before subjecting them to the Patio process; and on account of the additional expense of such roasting, only ores containing above 0·15% of silver can be worked with profit by this method. (Op. cit. p. 156.)

Influence of the state of division of the ore on amalgamation.—As previously mentioned, the ore of Zacatecas is not ground as finely as that of Guanaxuato, because the increase in the yield of silver does not pay for the extra cost of grinding. It ought to be stated, however, that most of the *haciendas* of Zacatecas treat the ore at a certain fixed rate, *maquila*, returning to the miner the silver produced, whilst at the *haciendas* of Guanaxuato the ore is actually bought from the miner. Hence, at the first-mentioned establishments, the quantity of ore treated will be the chief consideration, whilst, at the latter, not only the quantity of ore but its yield has to be considered. According

[1] The terms heat and cold seem to be here used in a specific technical sense, and to indicate quickness or slowness in the chemical reactions; and though there may be a rise in temperature proportionate to the intensity of those reactions, yet I doubt whether it is sufficiently sensible to have suggested the adoption of the terms heat and cold. It strikes me as more probable that these words are employed metaphorically, as is frequently the case. Thus we speak of a warm and cold heart without intending thereby to express an actual difference of temperature. In support of this view the following passage from Ward's Mexico (2nd ed. 1829. 2. p. 158) may be cited:—"The Mexican amalgamators explain this difference [*i.e.* as to the time and quantity of mercury, etc., required to amalgamate different ores] by their favourite terms of *minerales frios* (cold or sluggish minerals) and *minerales calientes* (hot ores, easily acted upon), and they attempt no more scientific solution of the changes which occur."

to Laur (op. cit. p. 120), the ore of Zacatecas contains a considerable proportion of complex sulphides of silver, which, in their raw state, even when ground to the highest degree of fineness, will not yield their silver in the Patio process.

Salt.—If salt is deficient in the *torta*, the reactions occur more slowly; but if it is used in excess, the reactions are energetic, follow each other rapidly, and the *torta* becomes neither too hot nor too cold. Often, however, this advantage in using an excess of salt is counterbalanced by the increased cost for this ingredient. A large excess of salt is said to cause loss by causing what is termed "flouring" of the mercury.[2] (See Newall's statement as to excess of salt, p. 610 antea.)

Magistral.—Some amalgamation-masters add the *magistral* at the same time as the salt, whilst others add it 24 hours afterwards. An excess of *magistral* causes heat in the *torta* and waste of mercury. As mentioned previously, the ores of Zacatecas and Fresnillo, which are rich in metallic sulphides, require a larger quantity of *magistral* (especially when containing galena) than those of Guanaxuato. When treating the first-mentioned ores, the *torta* is kept rather hot, and experienced amalgamation-masters have found that this state of the *torta* also answers well for the latter class of ores, on account of saving in time and increased yield in silver without any additional loss of mercury.

In the event of the *torta* becoming too cold, as indicated by the *tentadura*, more frequent *repasos*, or the addition of a further quantity of *magistral*, will remedy this evil; but, on the other hand, should the *torta* in the course of the process become too hot, it ought to be cooled either by leaving it at rest for a few days (*i.e.* without *repasos*), or by the addition of lime or wood-ashes and the concurrent suspension of *repasos* until the evil symptoms disappear. The first remedy (*i.e.* cessation of *repasos* for a few days) should be applied when ores rich in sulphides are under treatment, and the latter in the case of less sulphuretted ores. Mr. Newall states, on the contrary, that he has generally found a *repaso* after the intermixture of lime, when the *torta* is hot, to be very advantageous, as it prevents the stoppage of the *beneficio*; but this does not apply to *colorados* or to "hot ores." Sonneschmid urges that, when lime is used, it should be added in a very finely divided state, because, if used in coarse powder, there will be a risk of its cooling action continuing after the appearance of those signs which indicate that amalgamation is proceeding satisfactorily. (Op. cit. p. 219.) According to the same author, slimes of the residual ore, free from sulphates, have also been used for cooling the *torta*; but this practice has the disadvantage of greatly increasing the mass of the *torta*.

Napier states that copper, precipitated by metallic iron from solution of sulphate of copper, is used for cooling the *torta* in many amalgamation works and is preferred to lime; and it is supposed to act by converting cupric into cuprous chloride.[3] An excess of

[2] Laur, op. cit. p. 153. [3] Op. cit. p. 234.

copper would only temporarily check amalgamation and not lessen the yield of silver; but too much lime would completely stop amalgamation, and necessitate the addition of fresh *magistral*.

The addition of iron and zinc in the state of filings has also a cooling effect upon the *torta*; and their use has been found beneficial in lessening the consumption of mercury and increasing the yield of silver in the cases of ores rich in haloid salts of silver.

It is asserted that amalgamation-masters always dread the employment of these palliatives, because they retard the process and lessen the yield of silver, without reviving that portion of the mercury which has been uselessly attacked.[4]

Mercury.—If an excess of mercury has been added to the *torta*, the *limadura* becomes too fluid, and no proper judgment can be formed regarding the state of the amalgamation process; consequently it becomes necessary either to waste this excess of mercury by adding more *magistral*, or to save the mercury by washing the *torta* and recovering as much as possible of the silver from the residues.

Repasos.—Mr. H. Macintosh, at Guadalupe y Calvo, proved by comparative trials made with two *tortas* of the same weight and of the same ore-mixture, of which one was subjected to 8 *repasos* from 5 to 6 hours' duration, at intervals of from 3 to 4 days, and the other to the treading of the same number of mules day and night uninterruptedly, that there was a great saving of time in favour of the latter mode of proceeding; but whilst the yield in silver and loss of mercury were sensibly the same in both trials, double work of mules with a view of saving time was not considered advantageous. In the first instance amalgamation was completed in 27 days, and in the latter in 80 hours.

According to Laur, too frequent *repasos* cause the *limadura* to disappear, and so to deprive the amalgamation-master of his guide for the management of the process. In this case, in summer, with somewhat rich ores the *torta* must be left at rest for 2 or 3 days, when the *limadura* will reappear and the process again go on regularly; and, in a cold season and with poor ores, there is great risk of causing the *torta* to heat by frequent *repasos*. (Op. cit. p. 154.)

Beneficio de curtido.—This designation was applied to the Patio process when the mercury was not added to the ore-mud until several days after it had been mixed with salt and *magistral*. It was alleged, on the one hand, that this practice lessened the loss of mercury and increased the yield of silver; and, on the other hand, that it was attended with exactly contrary results. That it was not found to be advantageous may be inferred from the statement of Duport, that, when he published his work, it had been nearly quite abandoned. (Op. cit. p. 127.)

Rate at which amalgam is formed in successive stages of the process.—This is a point of much interest, and the following information respecting it is given by Laur. (Op. cit. pp. 156 et seq.) The for-

[4] Duport, p. 110.

mation of the silver amalgam does not take place at a uniformly progressive rate, but is very rapid at first and extremely slow towards the end of the process. Thus at Fresnillo, during the season of fine weather, it is not uncommon to see the first dose of mercury introduced into the *torta* wholly changed into dry amalgam in 48 hours after the beginning of the operation, and to contain $\frac{3}{4}$ of the total silver which will be extracted. The *azogueros* of Fresnillo state that with a docile ore, which ought to yield its silver in 12 days, half of the silver will be found in the mercury after the lapse of 2 days. Experiments on a *torta* of rich ores at Guanaxuato, which from the commencement of the process had received the whole of its mercury by September 28, gave the following results, the total silver which it should yield being represented by 100 :—

	Percentage of silver amalgamated.
October 11 (*i.e.* after 12 days)	92·79
„ 24	97·55
„ 26	98·84
„ 27	99·70
November 1 (*i.e.* after 33 days)	100·00

Copper-amalgam.—The application of copper-amalgam instead of pure mercury is stated to have been suggested and first carried into practice at Guadalupe y Calvo by a German, named Lukner; and is founded on the principle that the copper contained in the mercury reduces the chloride of silver supposed to be generated in the Patio process, and so prevents an equivalent proportion of mercury from being consumed in such reduction.[5] A patent was granted in Mexico to Messrs. Lukner and Henry Macintosh conjointly for the use of copper-amalgam ; but it is stated to have been evaded in many instances by employing precipitated copper instead of copper-amalgam.[6] Trials on the large scale proved that the best proportion of copper to add was 30% of the weight of the silver in the *torta*, as deduced from dry assays; and that is nearly in the proportion required by theory for the reduction of chloride of silver.

St. Clair Duport gives the following description of the process. The ore is mixed with $4\frac{1}{2}$% of its weight of salt from the Pacific coast, and then receives a *repaso*. After the lapse of 24 hours, mercury containing copper is added in such proportion that there may be $5\frac{1}{2}$ or 6 parts by weight of pure mercury and 0·30 or 0·33 of copper to 1 part of silver in the *torta*. Hence, the total silver in the *torta* must be accurately determined by assays. The cupriferous mercury is prepared by dissolving dry copper-amalgam in pure mercury; and is put into the *torta* along with an amount of sulphate of copper equal to $\frac{1}{4}$% of the weight of the ore. The *torta* is subjected to *repasos* every 2 or 3 days; and at the end of 3 or 4 weeks the operation is completed. There is no necessity for continual inspection as in the usual process of amalgamation. The liquid cupriferous mercury hardens as it lays hold of the silver in

[5] Duport, pp. 313 et seq. [6] Napier, op. cit. p. 234.

the ore; it loses its original dark colour and brightens as the copper contained in it is replaced by silver; and after 10 days, the amalgam obtained in the *tentaduras* precisely resembles that of the ordinary process when going on properly. After the *torta* has yielded its silver, it is treated in the usual manner. The ingots of silver contain gold and not more than from 2% to 4% of copper. The ore-mud from the *lavadero* or washing-house is further washed and yields a *schlich* of metallic sulphides of which copper-pyrites is the chief part. Copper-amalgam may be made from this *schlich*, by drying it in the air, roasting it in a reverberatory furnace, with the addition of 15% of common salt and 10% of green vitriol (ferrous sulphate), and treating the product, which contains chloride of copper (cupric chloride), in revolving wooden barrels (such as will be hereafter described under the head of Barrel Amalgamation), along with water, wrought-iron, and mercury. The barrels rotate 18 times per minute and continue in motion during about 24 hours. The charge for a barrel is composed as follows:—

Roasted *schlich*	1000 lbs.
Round bars of wrought-iron	200 „
Mercury	600 „

A very liquid amalgam is thus obtained, which yields by filtration about 500 lbs. of liquid mercury, and dry amalgam of copper and silver: its mean composition is as follows:—

Copper	72 lbs. 14 ozs.
Silver	4 „ 4 „
Mercury	619 „ 0 „

By the use of copper-amalgam the loss of mercury is reduced to about 5 ozs. per mark or 63% of the silver extracted.

According to Laur, experience at Guadalupe y Calvo has shown that the employment of copper-amalgam reduces the loss of mercury, and at the same time shortens the process, besides effecting a larger yield of silver.

Other amalgams.—Amalgams of zinc and lead have been tried in the case of sulphuretted ores, but not with satisfactory results.[7]

TREATMENT OF THE AMALGAMATED ORE.

According to Mr. Clement, in Zacatecas the amalgamated ore is conveyed to the washing-house in hand-barrows, with two men to each barrow. In this operation much dry horse-dung is used in order to prevent the mud from sticking to the barrows and wooden shovels with which it is laded. Great care is taken not to have the mud slimy, as in that case much would be thrown about or wasted. The washing-house (*lavadero*) contains one, two, or more vats.

Laur states that at Guanaxuato, before removing the ore-mud to the *lavadero*, it is made very liquid by throwing water on the *torta* and treading it with mules for 1½ or 2 hours; and that if the mercury is too ashy in colour (*couleur cendrée trop intense*), a little lime or

[7] Laur, op. cit. p. 204.

precipitated copper is previously added, by which means the mercury recovers its brightness: by the action of the *repaso*, under these conditions, such of the mercury as may be disseminated through the ore in extremely fine particles is aggregated into globules, capable of being separated from the mass by the subsequent washing. It is not indispensable, he thinks, to have recourse to the *baño*, as in Zacatecas, to collect together the fine particles of mercury, provided the *torta* contains 8 parts by weight of mercury to 1 of silver amalgamated; the liquidity of the amalgam, in this case, being sufficient to ensure its separation by suitable washing. (Op. cit. p. 169.)

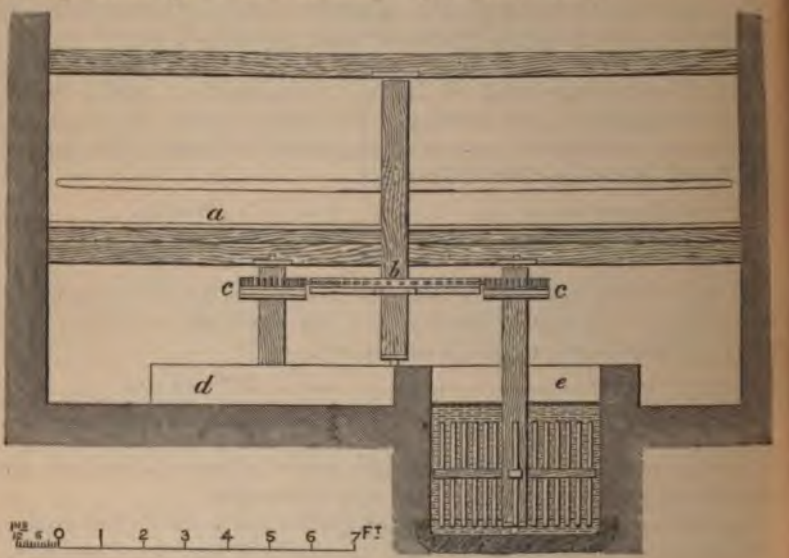

Fig. 93. Lavadero or Washing-house at Fresnillo. Copied from an engraving in Duport's treatise. There are two vats, placed side by side, one of which is shown in section: they are constructed of masonry. The stirring apparatus is worked by mules. The movement is more rapid than at Guanaxuato. In each vat 2½ *montones* of 20 quintals (2300 kil.) are washed per hour. The amalgam, almost entirely free from ore, is taken out from the bottom of the vat and does not need washing by hand. This method, though more expeditious, is much less perfect than that of Guanaxuato, and the washing of the residues on *planillas*, which is superfluous there, is indispensable, and produces much amalgam at Fresnillo.

a. Platform on which the mules walk.
b. Driving wheel.
c, c. Pinions at the upper part of the stirrer shaft.
d. Vat, which is circular, seen in elevation.
e. Vat seen in section.
f. Bottom of the vat formed out of a single block of porphyry.

At La Sauceda the vat or *tina* is circular, and is generally made of solid masonry encased with wood to the height of 2′ 6″ above the floor of the room; the bottom consists of a single stone, hollowed out into a cup-shaped cavity 9″ deep. The vat is 9′ in diameter and 7½′ in depth, inside measure. The length of the arms fixed crosswise to the shaft or spindle is 8′ 6″, and that of the upright dividers fixed to those arms is 6′. The lower ends of the dividers are 5″ above the bottom of the vat. The outlet is 18″ from the bottom, and is 6″ in diameter when new. (Clement.)

With regard to the process of washing in Zacatecas, Duport remarks that "the apparatus consisted only of a single vat (1843), and, owing to the comparative coarseness of the ore, it was necessary to communicate motion sufficiently violent to retain the particles in suspension; of which two causes the effect was the escape of a considerable quantity of amalgam along with the slime drawn off. A portion of the amalgam so removed was recovered by washing on the *planilla;* but this operation, besides its costliness, affords great facility for theft, and ends in being very unproductive."

Where there are two vats in the washing-house the *torta* is divided into 8 portions, of which one is washed at a time in each vat. Laur states that with two vats a *torta* of 78·2 tons is washed in Zacatecas in 18 hours during the summer, and in 24 hours during the winter season; tepid water, which may be had at a small cost in summer, much facilitating the re-uniting of the mercury and the amalgam. (Op. cit. p. 171.) This statement concerning tepid water is entirely new to Mr. Newall, who says that there is no apparatus in Zacatecas by which the water for the *lavadero* can be heated.

Laur states that in Zacatecas, after the washing of the last charge of ore-mud, men enter the vat and remove the residue, which consists of a little water, metallic sulphides, coarse grains of ore-amalgam, and mercury in excess; and that for this purpose they use small leather vessels, from which they pour it into basins often formed out of a single block of stone and placed a little above the floor of the *lavadero.* All these residues are then washed in large wooden dishes, at first with clean water, and afterwards, if necessary, with mercury; of which operation the products are mercury rich in silver, and residues charged with sulphides and containing mercury and grains of amalgam: these residues are reserved for subsequent treatment. (Op. cit. p. 171.)

In some places these vats are made of wood, and their tops are on a level with the floor; but such vats, it is stated, cause much mercury to be lost. The rotation of the shaft is effected by mules. The diameter of the mule-walk is 23′. Four mules work at a time, and during 4 hours consecutively. In washing they make 4 turns per minute, and 8 turns while the slime is being let off; and the shaft revolves 4 times as often, respectively, during those operations. The stuff washed per hour and per vat is 70 quintals (7100·9 lbs. a.v.d.). One man is engaged at each vat at 4*s.* 2*d.* per day; and each vat requires 12 mules of superior quality as to size, worth from 15*l.* to 20*l.* each.

At the Hacienda de Rocha, Guanaxuato, 4 vats are used for washing the amalgamated ore, and the operation is carried out as follows:— The vats are partially filled with water and the agitators set in motion. Into the first vat about 100 quintals of ore are gradually added, and this is repeated at intervals of 2 hours. Most of the amalgam settles in the 1st vat, from which the slimes pass consecutively into the 2nd, 3rd, and 4th vats, in the last of which almost all the suspended amalgam is collected. About 600 quintals

of ore are washed in these vats during 24 hours. After the whole of the *torta* has passed through the washing apparatus, the sediment collected at the bottom of the vats, consisting of amalgam and heavy *schlich*, and computed to be about $\frac{1}{5}$ of the weight of the ore, is transferred into wooden troughs about 39" (1 metre) in diameter and 19½" (0·5 metre) in depth, and then it is washed in bowls (*bateas*) in a large vat (*apuradora*) partially filled with water. The man who manages them leans over the tank, and with a hand on each side of the bowl communicates to the latter a peculiar shaking or rocking movement, at the same time constantly dipping up a small quantity of water, which he washes round the bowl and then throws out, and which carries along with it a portion of the *schlich*.[5] In this operation the amalgam is freed from the heavy *schlich* termed *relaves* or "washings," and the washed amalgam is carried in casks to the mercury store (*azogueria*), and kept there in a large stone trough (*pila*) having a very smooth inner surface. Sometimes from 3 to 4 quintals of mercury are added to the amalgam in the *pila* to render it quite liquid, when the mixture is stirred continually. During this operation fine particles of ore collect on the surface and are wiped off with flannel, to which the amalgam does not adhere. Finally the amalgam is repeatedly stirred up with the addition of a small quantity of clean water, until it shows a pure reflecting surface.

There are washed of amalgamated ore, per hour and per cubic metre of vat capacity, about 160 kilog. at the Hacienda de Bernardez, Zacatecas, and only 23 kilog. at the Hacienda de San Juan, Guanaxuato. The greater rapidity in the former locality lessens the cost of the operation, but the wash-water from the vats always carries off mercury and amalgam, which may be found in abundance in the residues. These losses either do not occur at Guanaxuato or appear to be insignificant, and this more than compensates for the greater slowness of the washing there. Hence Laur infers that the practice at Guanaxuato should be preferred to that of Zacatecas (op. cit. p. 174); but he does not seem to have taken into account the fact that the ore in this locality is much more finely ground than it is in Zacatecas, and that, consequently, it is not necessary to drive the stirring apparatus so rapidly as in the last locality, in order to keep the ore sufficiently suspended in the wash-water.

Treatment of the washed Amalgamated Ore.

In Zacatecas the earthy part of the ore from the *lavadero* is separated on the *planilla*, and there remains a *schlich*, termed *marmajas*, which consists chiefly of iron-pyrites and contains from 0·08% to 0·25% of silver. This *schlich* is roasted in a reverberatory furnace, ground in the *arrastre*, and then amalgamated. If amalgamated alone, the roasted *schlich* is stated to consume much mercury and yield scarcely half of its content of silver indicated by assay. [This, according to Mr. Newall, depends upon the roasting to which the *marmajas* have been subjected. A good oxidation in the furnace does not generally

[5] Napier, op. cit. p. 239.

tail a great loss of silver or mercury, when the *marmajas* are treated
ne, except in the case of such as are obtained from difficult or
bborn ores. The loss of silver ought not to exceed from 20% to
%, nor that of mercury from 16 to 18 ozs. per mark of silver.] Some
algamators assert that infinitely better results are obtained when
marmajas are mixed with 3 or 4 times their weight of ore pre-
usly to amalgamation.[2]

At Fresnillo the ore-mud, named *jales*, from the *lavadero*, con-
ned, according to numerous assays by Duport, 0·03% of silver,
ile the *schlich* or *marmajas* left after washing this ore-mud con-
ned about 0·1%. As this stuff was not rich enough to be smelted
th profit, it was subjected to additional washing, whereby the
idual earthy matter in the *marmajas*, amounting to about 15%
their weight, was removed, along with a large portion of but
ghtly argentiferous pyrites, and a second *schlich* (*polvillos*) was
tained, in which galena and the sulphides of silver, that had
aped amalgamation, predominated. This last *schlich* contained
m 0·2% to 0·3% of silver, and could be smelted with some profit.
is computed by Duport that in thus producing a *schlich* rich
ough in silver to be advantageously smelted, more than $\frac{4}{5}$ of the
ver originally present in the ore-mud or *jales* were lost.

At the Hacienda de Rocha the muddy water issuing from the last
t is run into slime-pits; the slimes deposited therein (*carcamos*) are
shed upon sleeping tables (*planillas*), and yield a very variable
antity of highly pyritic *schlich* termed *polvillos*. Usually the ore-
ssers receive in lieu of wages 25% of the silver resulting from the
algamation of the *polvillos*, which contain up to 0·3% of silver.

At Pachuca the slimes running to waste from the *planillas* first
ss over rotating round buddles, upon which a fine *schlich* con-
ning 0·2% of silver is collected.

Duport states that in Guanaxuato the *relaves* are re-ground in the
astre and yield some argentiferous amalgam rich in gold; but they
not again treated in the Patio process. In *relaves* proceeding
m the *lavadero*, in the treatment of ore containing 0·23% of silver,
port found by assay 0·06% of silver. It is worthy of note that
),000 lbs. of these *relaves*, by the second grinding in the *arrastre*,
duced only 52 lbs. of mercury and 15 marks of silver; so that
re remained in the waste-stuff thrown away sufficient silver to
rit attention from metallurgists. (Duport, op. cit. p. 228.) The
ne writer remarks that the allegations of the chief amalgamation-
sters, Mexican or foreign, concerning the poverty of their *relaves*,
not concordant; and it is natural that these men should for their
n credit desire to estimate the loss of silver as low as possible.
ere is, however, no doubt that the actual loss is very large.

Recently the *relaves* have been profitably treated by the Patera
cess (to be described in the sequel) at Guanavesi near Durango.[1]

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[1] Duport, op. cit. p. 250.

[2] Richter u. Hübner: Notizen über die Entsilberung von Amalgamationsrückständen durch den Patera Prozess in Guanavesi bei Durango. Preuss. Zeitschrift. 1873. p. 142.

TREATMENT OF THE AMALGAM.

The clean amalgam, according to Duport, is subjected to filtration in conical bags or *mangas*, of which the upper part is made of strong well-sewn leather, and the lower or pointed end of thick closely-woven canvas. Laur states that the bags are usually 6′ deep and 2′ in diameter at the mouth, which is fixed to a strong iron ring with chains attached for suspending the bag. The bags are suspended from a beam. At Fresnillo such bags or filters held from 2000 to 3000 lbs. of amalgam at a time. [The reduction *hacienda* at Fresnillo is not now in operation, as the company gave up working the mines some years ago.] The weight of the amalgam suffices to force through a considerable quantity of liquid mercury, which drops into a trough underneath lined with leather. Sometimes this liquid mercury, which still retains a small quantity of amalgam, has to undergo a second filtration through small filters made of fine linen. It may be estimated that usually the amalgam, which remains in the filter, consists of 1 part by weight of silver and 4 or 5 of mercury; and it is stated that the proportion of silver increases in a certain degree with the weight of the mass operated upon. Before filtration the amalgam at the top is much richer in silver than that in the middle, and richer still than that at the bottom, which often does not contain more than $\frac{1}{8}$th of its weight of silver. After 24 hours, with such a charge as that above-mentioned, the amalgam in the filter is extremely hard towards the top, where it contains about $\frac{1}{3}$ of its weight of silver; but remains very soft towards the point of the cone, where it still retains $\frac{1}{2}$ of its weight of mercury (Laur). With regard to the proportion of silver in the pressed amalgam, Laur's statement agrees with that of Duport; but Clement and Tilmann assert that the pressed amalgam in Zacatecas and Guanaxuato contains 44 and 45 marks of silver per 100 lbs., *i.e.* from 22% to 22·5%, respectively. Mr. Newall states that the proportion of silver varies with the class of ores, quality of grinding, amount of amalgam, etc.

Duport relates that in very dry weather, after several charges of amalgam have been consecutively operated upon, electric sparks escape from the iron ring, on which the leather of the bag is sewn, whenever any workman approaches it. Mr. Newall informs me that he has also observed this phenomenon, but that it is of rare occurrence.

TREATMENT OF THE PRESSED AMALGAM.

Distillation of the Amalgam.—The mercury is expelled from the pressed amalgam by heat, and the apparatus formerly used for this purpose was always a bell-shaped vessel of copper or iron[2] (*capellina*), surrounded by fuel on the outside: see fig. 94.

The pressed amalgam, on its removal from the filter, is broken up on tables covered with leather and having borders, after which

[2] Ward, op. cit. 2. p. 198.

it is beaten into moulds of wood or iron of the form of circular sectors, truncated at their summit, and from about 2″ to $2\frac{3}{8}$″ thick; and it is thus fashioned into similar and equal segments, termed *marquetas* or *bollos*, which weigh 30 lbs. each, and of which a certain number make a perfect disc, with a hole through the centre. A series of such discs is piled upon a metal stand, so as to form a cylin-

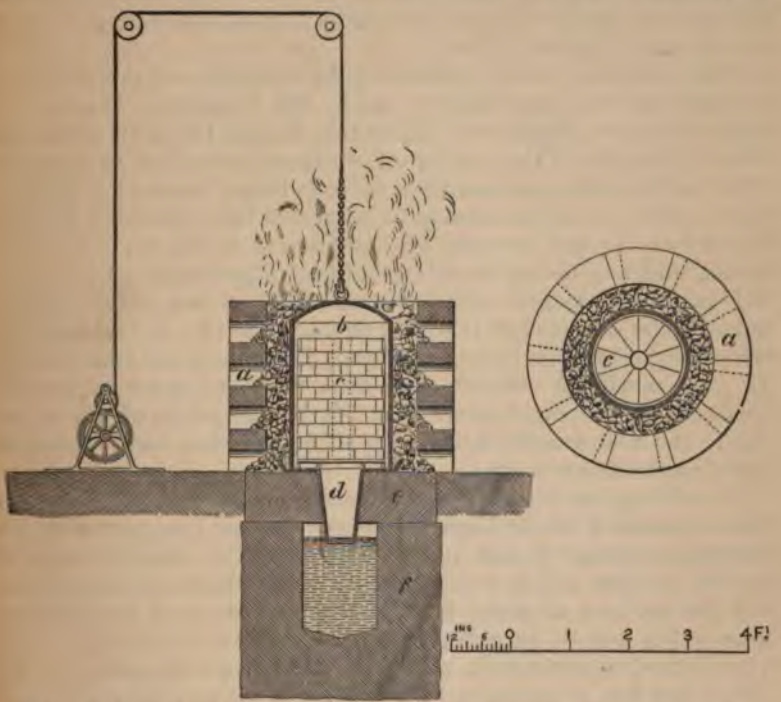

Fig. 94. *Capellina*, shown in section and in plan. Copied from an engraving in Duport's treatise.

a. Circular wall, with openings for the admission of air. In the space between the bell and it a charcoal fire is made. The circular wall consists only of blocks of fire-brick or stone set without mortar; it is taken down as the last charge of charcoal subsides, and is rebuilt at each operation.
b. Bell or *capellina*.
c Pile of amalgam resting upon an iron stand.
d. Copper vessel, on which the bell rests.
e. Stone, which supports *d*, and in which cavities are made for the circulation of water round *d*.
f. Reservoir of stone for receiving the mercury: it contains water which is being constantly changed during the operation.

The mouth of the bell is luted round to prevent the escape of mercurial vapour. Laur has given an engraving of a *capellina*, which differs only in a few minor details from that of Duport.

drical column or pile, termed *piña*, over which the *capellina* is lowered, and well luted round the base with a mixture of ashes, *saltierra*, and *lama*, or, according to Laur, with a slightly moist mixture of clay and wood-ashes. The charcoal round the exterior is then ignited, when the mercury is driven off, and condensed in the vessel underneath containing water, while the silver is left in the state of a spongy hard mass, retaining the original

shape of the pieces of amalgam. The firing lasts from 8 to 10 hours,[3] and, when carefully managed, the loss of mercury is insignificant, not exceeding 1 oz. (28·76 grammes) in 100 lbs. (46 kilog.) of mercury extracted; but, according to Laur, the average loss of mercury at the Hacienda de La Granja, Zacatecas, somewhat exceeds 5 ozs. in 100 lbs.: the average loss of mercury in 17 operations at this *hacienda*, with charges varying from 129·72 to 1327·56 kilog., was 1·87 kilog., the extremes being 1·38 and 2·76 kilog.: it was not in proportion to the charge. (Op. cit. p. 176.)

The following details concerning the distillation of the amalgam in Zacatecas were furnished to me by Mr. Clement:—The bell is made of copper alloyed with 2% of tin: it is 1′ 11″ in diameter and 3′ 7″ in height. The quantity of amalgam treated in 24 hours is 1250 marks, with a consumption of 2250 lbs. of charcoal including waste. The cost of charcoal is 1*s.* 8*d.* per 25 lbs. One man attends to the burning and receives, say, 14 reals or 7*s.* 7*d.* the job. The mould, used in pressing the amalgam into wedge-shaped pieces, holds 12½ marks of amalgam, containing about 22% of fine silver. After burning, the silver is left 11¾ in 12 fine, or even 12. In Guanaxuato, where larger bells are in use, 20 quintals of amalgam make one charge. In 1866, a charge consisting of from 50 to 60 cakes of pressed amalgam yielded in 12 hours from 500 to 600 marks of silver 998 fine;[4] and more recently a charge of 4000 marks has been treated in the same number of hours.[5]

According to Clemes, in Northern Mexico the *capellina* has been superseded in the large *haciendas* by a cast-iron retort on the Californian plan. This is about 4′ long and 10″ in diameter, circular or oval in bore, and is built horizontally in a small furnace, so that the fire can play all round it; the front end is closed by a plate or door which can be securely fastened on, and to the back end a small pipe is fitted to conduct the mercurial fumes to a condensing trough. About 800 lbs. of amalgam constitute a charge, and the retorting is generally completed in about 10 hours.

Casting the Silver into Bars.

Formerly it was required by the Mexican law that the gold and silver should be delivered to the government assay-offices in each district in the same state as they were obtained in the distillation process, and there, in the presence of the assayer, be melted and cast into bars of a given form not exceeding 136 marks in weight. The standard and the weight were then stamped upon the bars by the assayer in order to indicate their value and serve as the basis for levying the duties claimed by the State. If the owner of the bars objected to this decision with respect to value, he had the right of appealing to the Assayer-in-chief of the Central office in the city of

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[3] Napier says from 12 to 15 hours. Op. cit. p. 240.

[4] Der Bergbau und Amalgamations-Verfahren, etc., antea cit.

[5] Die Bergwerke, etc., antea cit.

Mexico, who alone had the power of altering it. But now nearly all the assay-offices of the State stamp the bars of known *haciendas* without remelting them, a practice not without risk, as shown by experience at the Mint of Durango. (Laur, op. cit. p. 177.)

The process of casting the silver at the Hacienda de La Sauceda, Zacatecas, is thus described in Lyon's work (2. p. 289). The silver is broken up with a wedge and sledge-hammer, as nearly as possible into pieces of the original segmental shape; and is sent to the melting-house in leather bags, each of which contains 135 marks. It is melted and cast into ingots, which by law ought not to exceed (1843) the weight of 136 marks (32·56 kilog.). The casting-house, or *casa de fundicion*, contains a common pair of furnace-bellows, of which the nozzle projects through a wall; and immediately in front of the nozzle is placed an iron cage, called *el craz*, which stands over a two-handled ladle to receive the metal as it melts. A charge of silver from the *capellina*, i.e. 135 marks, the quantity contained in one of the leathern sacks, is piled in this cage along with charcoal. The blast is let on, and fusion is completed in 23 minutes afterwards. The molten silver is poured into a stone or iron mould, called *ladrillera*, well lined with a preparation of fine clay. It is thus obtained in bars, in the form of pigs of lead, 17″ long, 6″ wide, and 2½″ deep, which are termed *barras de plata*. Each of these bars weighs, as nearly as possible, 135 marks or 1080 ozs. The foregoing description by Lyon, it should be recollected, applied to a period (1826) long anterior to the date of publication of St. Clair Duport's treatise. At Fresnillo fusion was effected in a reverberatory furnace, heated with wood. The roof is hemispherical. There are three flues to a furnace, one opposite the fireplace, and one on each side; which three flues unite in one above the roof. The height of the roof and the diameter of the bed are usually 1 metre. The charge is 270 marks of silver, which melts in less than ¾ of an hour, with a consumption of 25 lbs. of oak-wood. When fusion is complete, the furnace is tapped and the metal run into two ingot-moulds. In the melting of 2700 marks, witnessed by Duport, the difference in weight before and after the operation was not quite 5 marks (= 0·18%), thus showing how perfectly the mercury is distilled off in the *capellina*.[6] Laur, however, states that at the Bernardez Hacienda, Zacatecas, the silver by fusion loses, on the average, 1·07%, a loss attributed to the volatilization of mercury, though it is probably not wholly due to that cause. Silver derived from well-washed *tortas* is said to be fine, and to be accepted as such in mints (Lyon). Napier asserts that he has often seen silver extracted by the amalgamation process at Guanaxuato as fine as what is specially prepared in London for check-silver, *i.e.* fine silver to serve as a standard of comparison in assaying.[7] According to Mr. Newall, bar silver from the Patio process is generally 998 or 999 fine, and is seldom lower than 996.

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[6] Op. cit. p. 270.

[7] Op. cit. p. 240.

MODIFICATIONS OF THE PATIO PROCESS.

MODIFICATIONS OF THE PATIO PROCESS DUE TO THE NATURE OF THE ORE.—As previously intimated, the Patio process cannot be satisfactorily applied to ores which contain either a somewhat large proportion of haloid salts of silver, complex sulphuretted ores such as proustite and pyrargyrite, certain kinds of iron- or copper-pyrites unchangeable in the *patio*, grey copper-ore, bournonite, galena or argentiferous blende. But assuming that, owing to the content of silver in the ores or local circumstances, another process cannot be adopted, it is possible so to modify the Patio process as to obtain slightly better results, by the use of metallic amalgams in the case of ores of the complex *colorados* class impregnated with haloid salts of silver, and by a preliminary roasting of the ores which contain complex argentiferous sulphides.

Simple colorados.—According to Sonneschmid, many thousand quintals of silver ores, containing silver chiefly as a greenish variety of horn-silver (*i.e.* chloro-bromide), with some iron-pyrites and green oxide of copper (cupric carbonate?), have been successfully treated with salt and mercury alone. (Op. cit. p. 378.)

Complex colorados.—The presence of haloid salts of silver in the ores is indicated by the constant tendency of the *torta* to heat, by a considerable prolongation of the process, and by the very large losses of silver and mercury. In treating such ores in the *patio* the process is begun in the usual way; but when the first dose of mercury has been changed into amalgam, a few pounds of ferrous sulphate, which has become peroxidized by exposure to the air, are spread over the *torta*, and the second dose of mercury, in which zinc, lead, or copper has been dissolved, is added. The necessary quantity of metallic amalgam can only be ascertained by practice, as it depends not only on the quantity of haloid salt of silver present, but also on the quality of the magistral used and the state of the *torta*. An excess tends to increase the yield of silver and to preserve the mercury; but, on the other hand, such of the metal in the amalgam as is not consumed in the process will be found in the *plata piña* and necessitate its being refined before casting it into bars. Although the management of a *torta* thus treated is the same as usual, yet one point should be noted, and it is this: when, after the *repasos* which follow the introduction of the amalgam, the metallic *limadura* of the daily assays (*tentadura*) has disappeared, it must not, as in the ordinary working of the *torta*, be inferred that the ores have been exhausted of silver. In the case in question, especially if the proportion of chloride of silver is a little high, the *limadura*, an empirical sign of amalgamation in the case of sulphuretted ores, may disappear, and yet the mercury may continue to take up silver. Hence it becomes necessary to prolong the operation beyond what would have been required with sulphuretted ores, to make daily assays of the amalgam formed, and not to proceed to the washing until the content of silver in this amalgam has remained constant for at least two days. The use of these amalgams, in the case under consideration, shortens

he operation and much lessens the loss of mercury, but only slightly ncreases the yield of silver. Hence, when the ores are somewhat ich in chloride or bromide of silver, it is considered preferable to ubstitute the Cazo for the Patio process. (The foregoing account is nearly a literal translation from Laur, op. cit. pp. 202 et seq.)

Process at Charcas for the amalgamation of complex sulphuretted ores.—The various mineral species constituting the ores at Charcas have been found to contain the following proportions of silver per ent. :—

Antimonial grey-copper ore, without lead	0·750
Massive galena	0·570
Copper-pyrites.....	0·090
Light-brown blende.....	0·054
Antimonial galena and black compact blende ...	0·045
Arsenical iron-pyrites, apparently without copper-pyrites	0·020

The ores are not dressed, but sent to the amalgamation-works just as they come from the mine. A sample of a considerable lot of ore which had been crushed and ground yielded, by dry assay, 0·168% of silver. These ores in their raw state have proved wholly refractory in the *patio*, and cannot be treated by the Cazo process; and they contain too little lead to be smelted alone, and are too poor in silver to make it pay, in Mexico, to fetch plumbiferous matters from a distance. After numerous trials, the adventurers of Charcas have adopted the following method of treatment:—

I. Roasting the ground ore from the *arrastres* with 4% of the crude salts of Peñon Blanco.

II. Patio amalgamation, with 2½% more salt and 3½% of *magistral*.

The ore is crushed under stamps and ground in *arrastres*, and the ore-mud is poured on the *patio* floor and there left until it has become perfectly dried by the sun into hard masses, which are broken up with mallets and passed through sieves. The sifted ore is roasted in charges of 1800 lbs. during 12 hours at a very gentle heat, just sufficient to cause the combustion of the iron- and copper-pyrites. Roasting is effected in a furnace resembling a *magistral* furnace, but with a higher roof; and at some works the roasted ore is reground for several hours in *arrastres* in order to disintegrate the agglomerated lumps formed in roasting. The roasted ore is amalgamated in the *patio* in the usual way, and the operation is completed in 10 or 12 days. The loss of silver, exclusive of that in roasting, varies from 34% to 42%, and the loss of mercury is from 2 to 3·75 parts by weight to 1 of silver produced.

Process in Zacatecas for the amalgamation of complex ores.—The deep mines of Zacatecas produce massive sulphides which are unsuitable for direct amalgamation by the Patio process, The ore from the mine of Quebradilla consists of an intimate finely-granular mixture of argentite, pyrargyrite, much blende, galena, iron-pyrites, and very little copper-pyrites, in a greenish silicious gangue. If treated in its raw state by Patio amalgamation, this ore would require an enormous

quantity of *magistral*, the process would be greatly prolonged, the loss of mercury ruinous, and the yield of silver always very deficient; and for these reasons it is roasted prior to amalgamation. [Mr. Newall states that the Quebradilla ore is not considered difficult of reduction, that he does not think it contains blende in any large quantity, and that the ores at La Granja, the reduction works of this mine, are now seldom calcined.] The ore is ground in ordinary *arrastres*, then dried in the sun, and afterwards pulverized dry and sifted. It is now mixed with 1¼% of crude salt from the lake of Peñon Blanco, and roasted during 12 hours in a *magistral* furnace at a much higher temperature than in the roasting of copper-pyrites, on account of the large proportion of blende which it contains. After the first 4 hours' firing, when the ore should be at a bright red-heat, the temperature is lowered to redness, and during the remaining 8 hours the charge is rabbled as much as possible. The roasted ore is now amalgamated in the usual manner, with the addition of 6% of salt and 3¼% of *magistral* from Tepezalá. The loss of silver, exclusive of that in roasting, exceeds 20%, but the loss of mercury is less than in the amalgamation of the ordinary ores in a raw state.

In general it may be stated that with ores containing much blende, the best results will be obtained in the *patio* by previously roasting them for a long time, at a very gentle heat, with the addition of from 1% to 2% of salt. If the ores contain much iron- or copper-pyrites, or other kinds of pyritic copper ore, roasting will always a little increase the yield of silver; but this advantage will be generally counterbalanced in Mexico by the cost of roasting and the large loss of mercury. For such ores, at Real del Monte, Sombrerete, etc., the Barrel process has been substituted for that of Patio amalgamation. (The foregoing information concerning Charcas and Zacatecas is from Laur, op. cit. pp. 206 et seq.)

Amalgamation of the Sulphides obtained by washing on a Planilla the Residues from ordinary Tortas.—These residues, which are generally very rich in copper-pyrites, are roasted in a reverberatory furnace, but without the addition of common salt; and they are afterwards used as argentiferous *magistral* in the amalgamation of the raw ores. At certain *haciendas*, however, where the production of these residues is too considerable, they are treated by themselves in special *tortas* with the addition of 4% of salt, but no *magistral*, at the commencement of the process. The loss of silver, exclusive of that in roasting, exceeds 30%, and the loss of mercury is more by one-half than in the treatment of the ores from which these residues have proceeded. (Laur, op. cit. p. 214.) This statement, Mr. Newall remarks, cannot refer to Zacatecas, as the presence of copper is not common in the ores of that locality, and he thinks it must refer to Charcas.

Amalgamation of chlorinized sulphuretted Ores of Silver by the Patio Process.—Mr. J. H. Clemes, who is engaged at the Almada and Tirito Mines, Sonora, communicated to me in 1879 the following

observations made by himself concerning the treatment of sulphuretted ores of silver which had been subjected to a chlorinizing roasting with chloride of sodium. Having been assured by old *azogueros* that ores in which the silver is largely present as chloride give much trouble in the Patio process, he consulted metallurgical textbooks, but could find no reference to this difficulty. Although he has never himself treated any ores containing native chloride of silver, yet on one occasion he had to work a *torta* of ores which had been subjected to a thorough chlorinizing roasting in a reverberatory furnace. The finely-ground ores, which contained in their crude state 6% of copper as copper-pyrites and about 12% of galena, with an equal quantity of blende, and which assayed 0·1250% of silver (40 ozs. 16 dwts. 16 grs. per ton), were roasted with common salt in a long reverberatory furnace, and afterwards "leached," *i.e.* washed, with cold water, during 18 hours in order to remove any soluble chlorides of base metals. The leached ores, which assayed 0·1133% of silver (37 ozs. 0 dwt. 5 grs. per ton), were reground in order to break up clotted lumps formed during the roasting, and then treated in a *torta* containing about 12 tons. The *torta* was managed by a very intelligent and experienced *azoguero;* it received 600 lbs. of salt, and was incorporated with 75 lbs. of mercury. This mercury did not take up any silver worth mentioning in 22 days, although crystallized sulphate of copper had been added at each *repaso*, until at last the *torta* contained 161 lbs. of that salt. It may be asked why the copper-salt formed by roasting was leached out and the same salt added afterwards. The answer to this question is, that it was not possible to remove one soluble impurity without, at the same time, removing all. The same sized *torta* of "docile" ores, in which the silver is accompanied by carbonate of lead and a small quantity, say about 1½ or 2%, of carbonate of copper, would, with the same quantity of salt and *no* sulphate of copper, have needed from 12 to 13 arrobas (*i.e.* from 300 to 325 lbs.) of mercury.

In washing a small quantity of the *torta* composed of the chlorinized ores in the wooden bowl or *batea*, the light portions flowing over the rim assayed 0·090% of silver, and the mercury was just as liquid as when first added, though a little blackened by the salt of copper. An ordinary tailing from the "docile" ores would not have assayed more than 0·0197% of silver. The attempt to extract the silver from the chlorinized ores by the Patio process was then given up, and the *torta* treated in charges of 1250 lbs. in a Hepburn pan with 150 lbs. of mercury to each charge, the pulp being heated by blowing steam into it. [The Pan process will be fully described in the sequel.] The yield of the *torta* containing about 12 tons of ore was a bar of silver weighing 32·45 kilog. of 305 fine, this low "ley" (*i.e.* standard) being due to the large amount of sulphate of copper which had to be added to make the *torta* work. In Pan amalgamation the loss of mercury amounted to 4½ lbs. per ton of ore treated. It is said that these ores, when roasted without the addition of salt, will work in the *patio*, but that, owing to the subsequent introduction of Patera's

process, no trials were made with ores thus treated. Mr. Clemes concludes by stating that in his locality, if the nature of the ore requires a previous roasting, the silver which it contains can be more cheaply extracted by a solution of hyposulphite of lime (Patera's process), than by mercury either in pans or in the *patio*.

ESTUFA AMALGAMATION.—With the view of accelerating the amalgamation process at some *haciendas* situated in the colder and more rainy parts of Mexico, the *torta* is artificially heated during 2 or 3 days on a covered-in brick-floor having flues underneath, which arrangement is termed *estufa* or stove. Sonneschmid states that in this manner the process, with a very slight increase in the yield of silver, can be completed in from 8 to 14 days earlier than when the *torta* is continually left exposed to the weather; but that, on the other hand, the loss of mercury is increased by from 1 to 3 loths per centner of ore. Considering its cost, this process is, according to the same author, not to be recommended, and now is scarcely anywhere in use. Frézier stated early in the last century that at Puno and elsewhere in Peru a similar mode of treating the *torta* was in use.[8]

AMALGAMATION IN BARRELS.—Duport records the results of interesting experiments, which were made at Guadalupe y Calvo, concerning the treatment of the ground ore in barrels with the addition of the same reagents as in the Patio process; namely, common salt, sulphate of copper, and cupriferous mercury. The quantity of ore operated upon was 237 *cargas* (*i.e.* 71,100 lbs.). Each barrel contained 900 lbs. of ore, mixed with 10% of its weight of common salt and 0·25% of its weight of sulphate of copper, and continued during 24 hours in rotation. The proportion of copper in the mercury amounted to 50% of the total weight of the silver, as deduced from dry assays; and the weight of mercury in the barrel amounted to $\frac{2}{3}$ of that of the ore. Water was added in sufficient quantity to render the mud more liquid than in the Patio process.

TABLE OF THE RESULTS.

Number.	Weight of ore.		Content of silver in marks.	Silver extracted in marks.	Loss of mercury in ozs. per mark of silver.
	In cargas.	In lbs.			
1	32	9600	68	56	$8\frac{3}{4}$
2	12	3600	$19\frac{1}{2}$	19	$4\frac{1}{4}$
3	12	3600	26	19	3
4	16	4800	24	23	13
5	8	2400	12	9	$2\frac{1}{2}$
6	8	2400	$12\frac{1}{4}$	9	$2\frac{1}{2}$
7	18	5400	27	$19\frac{1}{2}$	$7\frac{1}{2}$
8	9	2700	$13\frac{1}{2}$	$10\frac{1}{2}$	$4\frac{1}{2}$
9	33	9900	66	$55\frac{1}{2}$	5
10	89	26,700	161	123	$6\frac{1}{2}$
	237	71,100	429	$343\frac{1}{2}$	...

[8] Voyage to the South Sea and along the Coasts of Chile and Peru, in the years 1712, 1713, and 1714. By M. Frézier Translation. London, 1717. p. 156.

The mean loss of silver, it will be perceived, was 20%, and of mercury about 6 ozs. per mark of silver extracted. During the course of these experiments, it was remarked that the quantity of water present greatly influenced the yield of silver and the loss of mercury. When the mud was very dry, the yield of silver was good, but the loss of mercury great; and when the mud was too liquid, opposite results were obtained. It was also found that after working the barrels during 6 or 7 hours, the greater part of the silver had combined with the mercury, and that subsequently the mercury continued to become very slowly richer in silver. It is asserted that owing to the irregularity of the results, and the much greater loss of silver,—on the average nearly double,—than in the Patio process when copper-amalgam was used, these experiments were abandoned, notwithstanding the advantages of shortening the time of operation, the less consumption of mercury, and the economy in avoiding the *repasos* of the Patio process, which were very expensive on account of the high price of forage.

LOSS OF METAL IN THE PATIO PROCESS.

Loss of mercury.—In Zacatecas, in the treatment of a *torta* containing 60 *montones* (of 2000 lbs. Spanish) of the ore previously mentioned, Mr. Clement found the loss of mercury to be 360 lbs. for 240 lbs. of silver extracted, *i.e.* $1\frac{1}{2}$ lb. of mercury for 1 lb. of silver extracted. The quantity of silver contained in the *torta*, according to assay, was 345 lbs., and, consequently, 105 lbs. remained unextracted.

A large portion of the mercury used is supposed to be converted into calomel, and what is so converted is designated *consumido*, *i.e.* the "consumed" or *chemically* lost in the process. Another portion is left in a finely-divided metallic state in the washed ore-mud, and may accordingly be described as *mechanically* lost. The weight of mercury "consumed" is estimated as equal in weight to the silver extracted, which, in the example given, amounted to 480 marks or 240 lbs. The total loss of mercury in that example was 360 lbs.; hence what was *mechanically* lost amounted to $360-240=120$ lbs., *i.e.* 4 ozs. per mark of silver. The loss of mercury, consequently, is 12 ozs. per mark of 8 ozs. of silver extracted, *i.e.* 8 ozs. *chemically* lost and 4 ozs. *mechanically* lost; or, as it may be stated, 1·5 by weight of mercury for 1 of silver. From the preceding data the total loss of mercury will be found to amount to 2 lbs. per ton of ore; and this is the general result in the amalgamation of the kind of ore specified. Duport records that during the last 7 months of 1839, in the amalgamation of ore from the *Veta Grande* lode in Zacatecas, the loss of mercury was $15\frac{1}{4}$ ozs. per mark of silver. He adds that in small establishments, this loss is often computed to exceed 18 ozs. per mark with ores but little tractable, particularly those which contain much galena. The explanation assigned for this fact is, that in the amalgamation process sulphide of lead seems to be partially changed into chloride, with equivalent destruction of *magistral*; and that, consequently, this agent must be used in larger

proportion, the result of which is greater action upon the mercury.' At Fresnillo, in 1840, the loss of mercury per mark of silver was $14\frac{1}{16}$ ozs.; in 1841, $12\frac{5}{16}$ ozs.; and in 1842, $11\frac{14}{16}$ ozs. The diminution in the consumption of mercury during 1841 and 1842 is ascribed in part to increasing care in conducting the amalgamation process, and in part to the abandonment, or at least greatly reduced working, of a lode, yielding ore charged with blende and galena, and therefore less amenable to treatment.[1]

According to Duport, amalgamation-masters regard it as an established and invariable principle, that the quantity of mercury which is irrecoverably lost or virtually destroyed, i.e. *consumido*, is equal in weight to the silver extracted. The loss of the other portion of the mercury, which is termed *perdida*, is mechanical in its nature and variable. Duport remarks that the above-mentioned principle relating to the *consumido* "is a prejudice so rooted amongst most of the amalgamation-masters that it is waste of time to argue with them on that point. The total deficit of mercury varies as much as from 10 to 24 ozs. per mark (8 ozs.) of silver extracted, according to the nature of the ore."[2] Laur reports that the loss of mercury for every 100 lbs. of silver extracted amounted in Zacatecas to 143 lbs. and in Guanaxuato to 162 lbs.; and as the ores operated upon at these two localities differed from each other both in quality and percentage of silver, he draws the conclusion that, excepting variations due to other circumstances of which the effect is very small, the consumption of mercury is always nearly proportionate to the quantity of silver produced. (Op. cit. p. 165.)

Loss of silver.—It has been stated by Mr. Clement that not less than 105 lbs. of silver remained unextracted in the 60 tons (of 2000 lbs.) of ore operated upon in Zacatecas; but a portion of this is recovered from the residual ore or "wastes." The residual ore is washed on a kind of nicking buddle, and about 6 tons of argentiferous product, consisting more or less of iron-pyrites and holding about 6 marks of silver, are returned to the works at the price of 4 reals (say 2*s.* 1*d.*) per *carga* of 300 lbs. This dressed pyritic product (*marmajas*) is calcined; and it is considered best to utilize it by adding it to the *tortas* during the winter months in the proportion of 5 tons at a time to each. It is estimated to yield 4 marks of silver per ton (of 2000 lbs.), when derived from ores containing 8 marks per ton, as determined from working a ton by itself. But some of this pyritic produce is employed as an adjunct in the preparation of *magistral*. In dressing the "wastes," some amalgam is obtained, say 4 ozs. per ton of original ore; and from the tail-races of the washing vats much amalgam is also recovered. The silver thus obtained from the "wastes" reduces the total loss of silver to 19%, the result of the *dry* assay of the ore being taken as the term of comparison: this loss is considered by Mr. Newall to be excessive.

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[1] Duport. op. cit. 252. [1] Ibid. p. 275.

[2] Ibid. p. 118.

Duport directs attention to the large quantity of silver lost in the residues or "wastes," after the separation of the *schlich* from them. These "wastes" contain from 0·07% to 0·12% of silver, and are thrown into the watercourses to be carried away with the first flood. [The modern "wastes" or *jales* have been carefully assayed by Mr. Newall, and have been seldom found to contain as much as 1 mark of silver per *monton*, i.e. 0·025%; but, in some of the old *jales*, he has found twice that amount of silver, though even this is rare.] It is difficult to reckon the marks of silver lost, in calculating the ore worked in Zacatecas, of which the residues retain from 15% to 40% of their original content of silver; for the assays made during several years of the *Veta Grande* ores (*i.e.* to which Mr. Clement's description applies), compared with the results of working the same ores in the Patio process, show differences of from 35% to 40%; while with the rich ores of the *San Clemente* and *San Nicolás* lodes, charged with native silver, the differences amount only to from 15% to 20%.[3] Mr. Newall asserts that the loss of from 35% to 40% is certainly excessive, and that of the ores existing in the Zacatecas district those of *San Clemente* and *San Nicolás* are about the most difficult to reduce. At Fresnillo, in 1839, the difference between the produce indicated by assay and the actual yield of silver was admitted to be 28%; and in 1841 and 1842, between 22% and 25%.[4] At Alamos, Sonora, Mr. Clemes assayed ores of 159 ozs. of silver per ton of 2000 lbs., containing much blende and galena, which he was assured yielded in the Patio process only from 50 to 60 ozs. of silver per ton.

According to Laur, the average losses of silver in the different districts are as follow:—In Guanaxuato, where the ores, which have a quartzose gangue, are free from blende, grey-copper ore, galena, and argentiferous copper-pyrites, and only contain silver either in the metallic state, as argentite, black antimonial sulphide (stephanite), or polybasite in very small proportion, the loss is from 12% to 13%.

In Zacatecas, where the ores are of a more complex composition, and are free from galena, grey-copper ore, and red silver ore, but charged with blende and iron- or copper-pyrites, the loss is stated to be 24·75%, which Mr. Newall regards as excessive. With ores containing red silver ore, such as those of the *Veta Grande* lode, the loss is much greater, and more or less proportionate to the quantity of that ore, which is declared to be absolutely irreducible by the Patio process.

At Fresnillo, where the ores have nearly the same composition as those of Zacatecas, but are less rich in silver, the loss exceeds 25%.

At Pachuca and Atotonilco el Chico, where the ores contain much blende, arsenical iron- and copper-pyrites, and a sensible quantity of galena and grey-copper ore, the loss exceeds 36%.

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[3] Duport, op. cit. p. 254.

[4] Op. cit. p. 274.

The losses above stated are, Laur says, certainly the *minima*, as in computing them no account was taken of the mercury in the silver from the *capellina*, or of the increase in weight of the ore from the wear of the stones in the *arrastre*, which is at least 2½% in Zacatecas, and as much as 10% when the *voladoras* consist of basalt.

Summing up the preceding statements of Mr. Clement, the loss of silver in treating in Zacatecas a *torta* of 60 tons of ore, containing 345 lbs. of silver by dry assay, is distributed as follows:—

	lbs.	Per cent.	lbs.	Per cent.
Original loss of silver in the Patio process			105	30·43
Deduct: silver recovered by the amalgamation of the *marmajas*	12·0	3·48		
Ditto from the amalgam in the "wastes"	27·5	7·95		
			39·5	11·43
Final loss of silver in the ore and amalgam retained by the *relaves* and "wastes"			65·5	19·00
			105·0	30·43

Particular attention is drawn to the comparatively very small amount of silver recovered from the *relaves* of the residual ore, and this fact justifies Duport's previous remark (p. 625 antea) that there remained in the waste-stuff thrown away sufficient silver to merit attention from metallurgists.

DELIVERY AND SALE OF ORES FOR THE PATIO PROCESS.

It frequently happens that capitalists in Mexico advance the necessary funds to the miners, and in some cases reserve to themselves the right to "beneficiate" the ores produced by the miner at a certain rate, which is fixed by the various *haciendas* and called *maquila*. This *maquila* includes all costs of "beneficiating" with the exception of that of the lost mercury, any excess of salt used above 2½%, and of the expense for any *repasos* exceeding 14 in number. The cost of these three items, and also of any metallic copper which may be required in the course of the process, has to be paid by the miner in addition to the *maquila*.

During the years 1862 and 1863 the *maquila* amounted, for instance, at Guanaxuato to $28 per *monton* of 32 quintals and $17½ per *monton* of 20 quintals, for ores containing on an average 6·69 marks per *monton*, i.e. 34 ozs. per ton; but in later years the *maquila* has been raised to $30 per *monton* of 32 quintals, in consequence of the higher prices ruling as regards fodder for the mules. It is stated that under these regulations large profits were realized by the *haciendas*.

According to Laur, while in former times the value of an ore used to be determined by inspection only, the prices now paid for ores are based upon the results of dry assays. At Guanaxuato payment is made according to the number of marks of fine silver contained in a *monton* of 32 quintals, but subject to the following deductions:—

For ores containing from	0 to 10 marks	: 4	marks.
„ „	10 to 15 „	: 4½	„
„ „	15 or more „	: 5	„

The remainder, multiplied by 6-eighths when ores contain from 0 to 30 marks, or by 5¾-eighths when containing 30 marks and above, gives the value in dollars to be paid for a *carga* of ore. Besides this sum, about 40% of the gold present in the ore is paid for. Hence it may be inferred that while silver ores, which are free from gold and yield by assay only 4 marks of silver per *monton*, i.e. 0·0625%, may be profitably treated by Patio amalgamation, they leave nothing for the expense of mining and carriage. Mr. Newall asserts that with average Zacatecas ore, 3 marks per *monton*, by assay, of silver alone (*i.e.* 0·075%) is amply sufficient to cover the cost of reduction, inclusive of profit for the *hacienda*.

COST OF TREATMENT OF THE PATIO PROCESS.

In Lyon's work is the following statement of the cost at the Hacienda de La Sauceda, Zacatecas, of amalgamating 1 *monton* of ore (= 2000 lbs. Spanish) containing 6 marks of silver (0·15% = 49 ozs. per ton), and allowing 1½ lb. of mercury to be lost per lb. of silver:—

	$	Reals.
Crushing 1 *monton* (= 2000 lbs.), at 1½ real per *carga* (of 300 lbs.)	1	2
Grinding in the *arrastre*, including allowance for wear and tear	1	5
Saltierra, 2½ *fanegas* at 7 reals	2	1½
Magistral, 3 *arrobas* (of 25 lbs. each) at $4 per *carga*	1	0
Repasos, 10 at 1 real each	1	2
Washing, 1 *monton*	0	3
Burning the silver, *i.e.* driving off mercury from the amalgam	0	2
Wages	1	0
Mercury consumed and lost, 4 lbs. 8 ozs. at 6 reals per lb.	3	3
	12	2½*

* In Mexico 8 reals = 1 dollar.

As the ores increase in richness the cost is higher, in the proportion of 8 ozs. of mercury for every additional mark of silver. Thus ores of 26 marks per *monton* would cost 7½ dollars more than stated above, which is equal to 10 lbs. of mercury in value. According to Ward, the average cost of amalgamating 1 *monton* of ore at the same establishment was equal to the value of 12 ozs. Spanish of silver (1 oz. Spanish = 443·8 grains English). (Op. cit. 2. p. 339.)

The following comparative statement of the cost of the Patio process in Zacatecas for ores yielding 0·123% (40 ozs. per ton) of silver, and in Guanaxuato for ores yielding 0·09% (29 ozs. per ton) of silver, has been extracted from Laur's paper:—

	Per metrical ton (0·984 ton English).	
	Zacatecas.	Guanaxuato.
	$	$
Stamping	1·03	1·28
Grinding	2·56	5·58
Carried forward	$ 3·59	$ 6.86

	Per metrical ton (0·984 ton English). Zacatecas.		Guanaxuato.
	$		$
Brought forward	3·59		6·86
Patio amalgamation;—	$	$	
Wages ..... 0·63		..... 0·63	
Mules..... 0·28		..... 0·57	
Salt..... 2·07		..... 2·45	
Mercury..... 2·25		..... 2·08	
Magistral..... 0·46	5·76	..... 1·69	7·53
Lime ..... 0·01		Sulphate of copper . 0·06 Cement copper.....	
Miscellaneous..... 0·06		..... 0·05	
Washing the *torta*	0·51	.....	0·72
Distillation, and melting of silver	0·18	.....	0·14
Dressing of residues	0·02	.....	0·12
General expenses.....	1·71	.....	0·99
Total.....	$11·77		$16·36

The prices of labour and of the chief materials were in—

	Zacatecas.	Guanaxuato.
	$ per day.	$ per day.
Labour:—		
Azoguero	5	 5
Foreman	1	 1
Common labourer	0·5	.... 0·5
Materials:—		
Mercury, per Spanish quintal.....	58	 64
Salt containing 70% of chloride of sodium, per *carga* .	8·125	.... 8·25*
Magistral, per *carga*	5·17	.... 13·05
Maize in grain, per *fanega* (1·96 cub. ft. Engl.)	2·25	.... 2·5
Straw or fodder, per *carga*	1·5	.... 2·625

* The average price of sea-salt (containing about 92% of chloride of sodium) was at the time as high as $15 per *carga*; but now (1879), according to Mr. Newall, it is from $3 to $2½ per *carga*, containing 90% of chloride of sodium

According to Mr. Petherick, at Fresnillo the cost of treating ores, yielding from $40·48 to $51·70 worth of silver per ton, varied during 1840 to 1842 from $17·05 to $20·78 per ton of 2000 lbs.

Besides the prices of the three chief substances used in the Patio process—salt, *magistral*, and mercury—the price of the fodder for the horses and mules has a considerable influence upon the total cost of the Patio process, and it is subject to considerable fluctuation. Laur makes the following statement concerning the cost of motive power, *i.e.* of mules, in stamping and grinding the ore, for good, average, and bad harvests:—

Harvest.	Price of fodder.		Cost for stamping and grinding per metr. ton of ore.
	Maize, per *fanega*.	Hay and straw, per *arroba*.	
	$	Reals.	$
Good	1	1	1·57
Average.....	2¾	1	1·84
Bad.....	9	5	7·42

ıe expense of *repasos* increases in the same ratio from $0·27 to 1·08 per metrical ton; consequently the total extra cost of the tio process, with fodder prices ruling during a bad harvest, would $6·39 per metrical ton, or $78,224 for 10,680 metrical tons of ore ated at the Bernardez Hacienda, Zacatecas, during one year; a sum ite sufficient to convert a reasonable profit into a serious loss.

The fixed expenses (*dépenses fixes*) of the Patio process are computed Duport at $14 per *monton* of 2000 lbs. (920 kilog. of ore). However, at Fresnillo and in Guanaxuato they amounted to $13 per *nton*; and the reason assigned for the difference is that in these calities the interest of the capital expended in stores of every kind, ıd of the money paid in advance for labour during the operation, is ot included in the account. The average consumption of mercury taken at 13 ozs. per mark of silver obtained. The average content f silver in the ores is taken at 0·2 per cent.; and is founded on the ields of silver in the following districts:—

Guanaxuato		0·19
Fresnillo		0·15
Zacatecas	Veta Grande	0·20
	San Clemente	0·46
Tasco		0·15
Guadalupe y Calvo		0·25

ıe mean of these numbers is 0·23 per cent., which Duport con- lers it necessary to reduce to 0·20, because among the districts hich had produced much silver in recent years (*i.e.* prior to 1843), e former number had not been reached at Fresnillo. According to on Fausto d'Elhuyar, the average percentage of silver in the ores ised in Mexico at the beginning of the present century varied from 18 to 0·25, which, it will be seen, is nearly the same as at the bsequent period mentioned by Duport.[5]

It is necessary to inform the reader that although the "exploita- on" of the mines is free in Mexico, yet the adventurers cannot freely spose of the gold and silver which they have produced. Both metals leaving the *haciendas* must be delivered to the Assay-office esta- ished by the State in each district, and there be cast into bars, hich are weighed and assayed. From the Assay-office the bars are nveyed to the Mint in order to be coined, which was formerly ligatory, the law forbidding all exportation of gold and silver in rs. At this time when the exchange for specie takes place the ties charged by the State are levied. The coin may now pass into rculation in the locality; but if it be desired to send it beyond the ate, a declaration to that effect must be made, and a duty of ¼% in me of the States paid for such permission to circulate. If it be tended to export coin, it must pass through the Custom-house and y a further duty of 5% to the Federal Government, to which must added the expenses of commission, freight, and insurance before it n reach the markets of the Old World. Although silver in bars

[5] Humboldt, Nouvelle Espagne, 1811. 2. p. 512.

may now be exported, yet it is charged with the same Mint dues : in the case of actual coinage. These items together amount to a ve large proportion of the value of the metals; and, with respect to t mineral industry of the country, are equivalent to a considera improvement of the ores raised.[6]

Laur states that the government taxes, inclusive of coina expenses amounting to 11·1 per cent., have to be paid, when the b of silver from the *haciendas* are exchanged at the Mints for coin; a further that the charges upon the silver bars from the time of leavi the *hacienda* until their arrival at the money markets of Europe as follow :—

	Per cent.
Government taxes, inclusive of coinage	11·100
Circulation tax.....	2·000
Export duty	6·000
Commercial expenses	4·125
Total per cent. of the value of the silver.....	23·225

Duport has presented, in the following table, the total charges grammes of fine silver on the extraction of a kilogramme of fi silver.

	Grammes of fine silver.		Grammes of fine silver.	Grammes fine silve
Duty on coinage	45	Government taxes, inclusive of coinage.....		90
Duty on the ingots	45			
Cost of melting and assaying before coinage				10
Mercury (consumption estimated at 13 ozs. per mark, *i.e.* 1625 grammes per kilogramme) at $130 per Mexican quintal. One dollar contains 24·421 grammes of fine silver,—$130=3174·730 grammes of fine silver. One Mexican quintal=45·976 kilogrammes		.....	112·00	454
Rent.....	17·10	Rent and management	37·62	
Management.....	20·52			
Stamps.....	34·20	Trituration.....	171·00	
Arrastres	136·80			
Labour in the Patio process.....	47·88	Treatment of ground ore	71·82	
Washing	10·26			
Distillation of amalgam .	13·68			
Magistral and salt			61·56	
Remaining for raising ore and for profit				446
				1000

In the event of exportation, the following items of cost must added :—

[6] Laur, op. cit. p. 297. [7] Idem.

	Grammes of fine silver.
Export duty	35
Tax on entry at the port	20
Carriage to the sea, commission, etc.	25
	80

The residue of 446 grammes of fine silver is equivalent to $18·27. Taking the yield of silver at 0·2 per cent. of the ore, the quantity of ore required to produce 1 kilogramme of silver is 500 kilogrammes = 1087 lbs. Spanish. Hence $5·04 per *carga* of 300 lbs. of ore, the weight generally preferred in estimating the price of the ore, represents the amount available for the raising or purchasing of ore and for profit after deducting interest on capital. But taking the average yield of silver to be only 0·1 per cent., as appears to be nearer the truth at present, for $5·04 it is necessary to substitute $2·52.

On the subject of the existing Government exactions in Mexico Laur makes the following comments, which appear to me to be sound and judicious:—"Of the Mining Code which Spain gave to her colonies, the wise regulations for the underground working, which would have prevented so much ruin, have been allowed to lapse, while the fiscal measures, which were taken in order to protect the rights of the Crown with respect to the produce of the mines, have been retained with the utmost rigour. These measures, further aggravated by the different governments which have succeeded to the Spanish dominion, weigh heavily at present upon the mineral industry, and form perhaps the most serious obstacle to its progress."

NOTES BY MR. WILLIAM JAMES NEWALL ON THE PRECEDING ARTICLE ON THE PATIO PROCESS, APRIL 1879.

The date of my information on the subject, which relates almost entirely to Zacatecas, is from 1871 to 1878.

Some advances and improvements have been made in the Patio process since the date of the greater part of the information contained in the preceding article, but not a moiety of what might have been expected if capitalists in Mexico were less timid in introducing innovations, and if amalgamation-masters were less conservative in their traditional knowledge. These latter form a powerful clique, and it is only in late years that the mystery with which they surrounded the process is being gradually dispelled by the influential means of the titled professors and engineers of the Mining College of Mexico. The members and pupils of this College are now pursuing a scientific study of the phenomena of the process, and it is to be hoped that capitalists will soon pay more attention to mechanical improvements in the machinery and useful innovations in the amalgamation.

Dry Grinding (*Granzeo*).—This is now almost entirely done by Chilean mills, instead of stamps. A new mill of this class, intro-

duced very lately into Guanajuato, and only tried in Zacatecas last year, deserves description. It consists of a large stone wheel, encased in cast-iron, about 4" thick, rolling round a vertical wooden shaft, on a bottom also of cast-iron. The case of the wheel is composed of 6 segments, with flanges for screw-bolts to hold them together; they thus form the circumference of the wheel. Each of these segments is about $1\frac{1}{2}'$ wide and $2\frac{1}{2}'$ long. The blocks for the ring on which the wheel rolls, 8 in number, are also of about the same length, thickness, and breadth, but flat. Thus the diameter of the wheel is about 5', and that of the outer circle of the bottom ring about 7'. The weight of the iron alone is about 100 quintals, or 10,000 lbs., while that of the stone varies. These mills are erected either on arches, or on a high piece of ground, so that a small chamber remains under the centre of the mill. Each mill is driven by 3 mules. To the vertical revolving shaft (in which also revolves the head of the horizontal shaft of the wheel, to which the mules are directly attached) is fastened a conical sieve, somewhat like an opened umbrella. As the wheel goes over the ore, the latter is shovelled up on the sieve by a boy. The ground ore passes through the sieve and falls into the chamber below, whilst the larger particles roll down the incline of the sieve and fall into the track of the wheel. The holes on the umbrella-like sieve are not generally more than $\frac{1}{2}$" in diameter. I cannot now give a statement of the amount of work done by these mills, as I am entirely writing from memory, without the help of a single note.

Wet Grinding (*Molienda*).—The *granza* is put into the *tahonas* at sunrise every day, and not discharged into the *patio* until the next morning, the work being constant. The amount of *granza* put into each *tahona* is 10 quintals; and into each *arrastre*, or gold *tahona*, 8 or 6. The work of charging and discharging the *tahonas* is very tedious and wasteful in labour, all the carrying being on men's shoulders, and the weighing being done with steelyards. It is generally over before the heat of the day begins, at 8 A.M., commencing at between 4 and 5 A.M.

Patio.—The mud discharged into the tank formed in the *patio* is called a *lamero*, and does not become a *torta* until it has received the mercury. After the requisite number of *montones* has been collected, and for which there is no absolute rule, the mud is well mixed by the treading of horses. After mixing, a sample is carefully taken out and assayed by at least two different assayers, after which the salt is added. Great attention is now paid to the quality of the substances used in the Patio process, and analyses of them are generally made before any contract is concluded.

Salt.—The quantity of salt per *monton* varies very little, each *hacienda* generally having determined on a fixed amount to be added to all the ores reduced in it, and at all seasons. Four *arrobas* per *monton* of 2000 lbs. Spanish is a fair average for all the Zacatecas *haciendas*.

Magistral.—I have found that, as a rule, not more than from 50% to 70% of the copper in the raw *magistral* is converted into sul-

phate in the process of roasting. Some old-fashioned amalgamation-masters object to using too good a *magistral*, as they are more liable to spoil a *torta* by adding an excess of good *magistral*, than of weak and inferior stuff, especially if the ore is docile or "hot." The heat given out by newly-roasted *magistral* must be almost entirely due to the presence of anhydrous sulphates, and merely serves as a guide as to its quality. This physical heat does undoubtedly give a quick but temporary impulse to the amalgamation, often causing the mercury to be attacked, and lasting only during the hydration of the *magistral*. To this the name of *piquete* (sting) has been given, and *azogueros* who are accustomed to it miss it when the *magistral* has been exposed to the air, and often declare it unserviceable when it is really not so. Crystallized sulphate of copper seems to me a better agent than *magistral*, as the absence of *piquete* enables one to determine at once the quantity required for a *torta*, the action being more continuous and sustained, whereby the frequent additions of *magistral*, with its transient *piquetes*, are avoided.

Incorporo.—This is now generally made, in Zacatecas, with 3 lbs. of mercury per mark of silver that the *torta* is expected to give. It has been found that one mark of silver will dry this amount of mercury.

Repasos.—The treading is always done with horses in Zacatecas, or with men when the *tortas* are too small, or the ore contains an excess of sulphates. In Guanajuato mules are used, as horses are much dearer than in Zacatecas. There is no rule as to when a *repaso* or a "rest" should be given to a *torta*, as it all depends upon the course of the *beneficio*. A day's, or even two days', rest is sometimes very useful. Many mechanical substitutes have been tried; but, as a rule, they have not proved as satisfactory as the animals. Until an apparatus is invented that should not only mix the ore thoroughly, but produce as much friction as the horses' hoofs, I think the present system will hold its position. When men are employed, they do not merely tread the *torta* as in ordinary walking, but are taught to raise the leg considerably, throw it forward, and draw the sole of the foot backwards as it passes through the muddy mass to the floor underneath; by which practice, it will be perceived, intermixture of the ingredients of the *torta* must be greatly promoted.

Baño.—This is added the day the *torta* is to be washed, and serves to collect all the *pasilla* and globules of mercury. Should the amalgam in the *torta* be very dry, a small preparatory *baño* is sometimes added a day or two before the final *baño*, and *repasos* given. Sometimes the *baño* is not put into the *torta* at all, but into the vat (*tina*) of the *lavadero*. This is, I believe, the usual custom in Guanajuato now, especially when the *camon* is used. The *camon* is merely a duct leading from the *torta* to the *lavadero*, along which the ore-mud is pushed or drawn, having been previously made of the consistency of thick gruel.

I may here observe, that a great difference exists in the nature of the Guanajuato and Zacatecas ores, and that to this difference is to be attributed the almost incomprehensible divergence that exists between the Guanajuato and Zacatecas systems. In the first place,

the quality of the ores varies but slightly, gold being always present, and the metalliferous compounds being simpler and less abundant than in Zacatecas. In order to collect the gold in the *arrastres*, the ore is ground much finer in Guanajuato; and this, combined with the comparative absence of other metals and the presence of a large amount of earthy gangue, makes the ore-mud very sticky or clayey (*lamoso*). For this reason three *tinas* (vats) are required in the Guanajuato *lavadero*, before the amalgam can be separated from the mud; the *tortas* must be thinner than in Zacatecas for the *repasos*, and the yield of *marmajas* is almost *nil*.

In Zacatecas the variety of metallic compounds is very large, and, with the exception of some *colorados*, the gangue is generally dry (*seco*), or the contrary to *lamoso*. The metalliferous part of the ores is sometimes enormous, notably so in the second zone mentioned in my note, where sometimes more than half the gangue is metallic. It will at once be seen why one *tina* suffices in the Zacatecas *lavadero*, and the *camon* is undesirable.

AMALGAMATION.—To properly describe the different appearances of the mercury and amalgam in the *tentaduras* of the Patio, is almost an impossibility, as there is an almost infinite variety of phenomena. Every ore appears to require a different treatment, and every amalgamation-master has a method, more or less, of his own. It is therefore not to be wondered at if statements as to the Patio process appear contradictory. I can only give here my own experience on the subject, extending over a period of eight years' almost uninterrupted careful and methodical observations on various classes of Zacatecas ore. I will now describe the usual appearances of a good *beneficio*, of average *negro* ores, without accidents of any kind. The description on page 601 seems to me correct as far as it goes, and what I say here is meant more as an appendix to it.

When the mercury has been added to the *torta*, and in the first *tentadura*, the appearances of a good *incorporo* are as follow:—The mercury will be found subdivided into numerous globules of different sizes, extending from the smallest at the top, to the larger ones at the bottom of the *schlich*. The floured mercury at the top is called the *ceja* (eyebrow), and, on gentle pressure, the globules have a certain amount of attraction for each other, and, forming oval-shaped globules of larger sizes, roll down slowly to the bottom; some minute globules will adhere to each other and form a kind of chain: hence the Spanish name given to this appearance, viz. *encadene* (substantive in Spanish) and *encadenar* (verb in Spanish). Should more pressure be applied to these oval and chain-like formations, part of the mercury will adhere to the ball of the thumb; and on slightly rubbing, the globules will assume their natural shape, and, joining, form one large globule. The colour of this should be of a slight pearl-grey, which ought, as nearly as possible, to be maintained throughout the *beneficio*. With some ores this is impossible; and when crystallized sulphate of copper is used, the *cuerpo* (globule) is generally of a very light yellow tinge. In these last cases the colour of the *ceja*, *liz*, or *limadura* should be pearl-grey.

When the 3 lbs. of mercury per mark are added at once, silver amalgam will not appear in the *ceja* until the fourth or fifth day, and sometimes not at all. In this latter case the *torta* is said to proceed *en el cuerpo*. The day after a good *incorporo*, such as described, the mercury will be found in one globule with some silver amalgam, and the *ceja* will have almost disappeared, what remains being merely *desecho*, or floured mercury, which should collect easily into globules on rubbing gently. The amalgam in the globule should be brilliant, firm, and of a slightly grey tinge (very much like the silvering of looking-glasses). In subsequent days, the *ceja* should pass from *desecho* of mercury into dry amalgam, *limadura*, accurately described by Duport on page 614. The *schlich* should also contain *pasilla*, or amalgam in irregular pieces. The size of the *limadura* increases until about the middle of the *beneficio*, when the globule becomes less fluid from the increased amount of amalgam which it contains. The *cuerpo* is then said to be *borracho* (drunk or intoxicated), because of its sluggish, irregular movement in rolling about the vanning horn. From this period to the end of the *beneficio*, the *limadura* gradually diminishes in size until the thin film of *desecho*, as on the first day after the *incorporo*, replaces it. The *torta* is then *rendida* (conquered), and the *liz*, or *ceja*, is said to *chorrear* (drop). The amalgam is found in the *schlich* in irregular pieces, all the mercury having been dried up by the silver. When the *baño* is added, the *ceja* of *desecho* disappears almost entirely, and the amalgam is collected in one large globule of mercury of a natural colour. The *torta* is then carefully smoothed over, and the surrounding *patio* swept, the men commencing to carry the mud to the *lavadero*. The *beneficio* above described is what may be termed the acme of the Patio process, and, as such, is most difficult of attainment. It is but seldom that I have seen a *torta* beneficiated thus, and the variety of phenomena one sees is astounding: two *tortas* of the same ore taken from the same heap will often show wide and unaccountable divergence in their behaviour under treatment. I feel convinced that, if such a *beneficio* could always be attained, the loss of mercury would not average more than 9 or 10 ozs. per mark of silver produced; that of silver more than from 8 to 12 per cent., and the number of days in *beneficio* more than from 8 to 10. The percentage of the loss of silver seems to me as very much overstated in the different accounts given in the preceding pages; but the facts, that no assays of the *lamero* were made at the time mentioned, and that little care was taken of the quality of the materials used in the amalgamation, may explain this. Referring to my note on page 636, I may here mention what would now be considered as a fair average high loss for the different classes of Zacatecas ores:—

Ores from 2nd zone, rebellious, containing galena, pyrites, etc.	20% or 25%
Ores from 1st zone, medium, containing less galena, pyrites, and ruby silver	20%
Ores from 3rd zone, docile, containing "blue silver" and little galena	15%

In some quartzose and slatey ores of the third zone the loss of silver averages only 10%: in one class of these ores the loss of mercury for a long period did not exceed from 7 ozs. to 8 ozs., showing that in this case the *consumido* was less than weight for weight. In some of the *colorado* ores the loss of silver does sometimes reach 40%; but this is now considered exceptional, and 33% for such ores is termed a heavy average loss. We must bear in mind that all these estimates of loss of silver are only made on what may be called the first stage of the Patio process, and that the silver afterwards obtained from the *carcamo*, the *planillas*, and the *marmajas*, is not included in the product of a *torta*. If some accurate observations were made on this subject, I believe the ultimate actual loss of silver, by the Patio process, would be found much smaller than what it is imagined to be, even by the staunchest advocates of this process. Its adaptability is also wonderful, and I believe that, with patient and careful study, almost any ore can be reduced in its crude state, as long as it does not contain an excess of zinc, antimony, arsenic, and chloro-bromide of silver.

Marmajas.—This is the next subject on which some further remarks may be of interest. The treatment of these, and the result, depend entirely upon the class of ores that produces them, and, as a rule, amalgamation-masters prefer to add them to the *tortas* of crude ore. When they are properly calcined, the difficulty of reducing them separately is not so very great, unless, in the calcination, large amounts of copper-pyrites have been converted into sulphates. I have seen reduced many *tortas* of *marmajas* from Zacatecas ores, and the loss of silver has seldom exceeded 30%, unless the calcination has been palpably bad, whilst sometimes it has been as low as 15%. On the other hand, the loss of mercury is seldom less than 16 ozs. per mark of silver. It must be remarked that the residue of the *marmajas* also passes through the *planillas*, so that really only the *jales* are thrown away. For some years I regularly assayed the *jales*, and the average percentage of silver in those that were thrown into the waste-heap was about 0·015. In Fresnillo, great and notorious carelessness was shown in this branch of the process, the *schlich* being frequently not separated from the *jales*, and the washing and grinding hurried. I am at present occupied in reducing these *jales*, and yet I cannot count on a higher average percentage of silver than from 0·0375 to 0·04375 ($1\frac{1}{2}$ and $1\frac{3}{4}$ mark per *monton*). I have also assayed numerous samples of *jales*, in and about Zacatecas, with a view to reducing them; and although 0·05% of silver would leave a margin for profit, I have been unable to find *jales* of this percentage in sufficient quantity to undertake their reduction, even in old waste-heaps of bygone *bonanzas*. It is true that the majority of these have been washed away by the floods, and I only allude here to those that still exist, but which one can infer as unlikely to be different from the ones washed away. The statement of Duport, on p. 637, that *jales* contain as much as from 0·07% to 0·12% of silver, therefore, seems to me exaggerated in referring to

Zacatecas and Fresnillo, the only two places on which I can speak with any authority.

PATIO PROCESS AS CONDUCTED IN SOUTH AMERICA.[*]

Nature and Mode of Occurrence of the Ores.

Most of the silver lodes of South America occur along the eastern declivity of the Southern Andes, chiefly in rocks of the Jurassic age, which are represented there by various kinds of limestone, sandstone, and conglomerate. These lodes are also found, though rarely, in porphyry, which, in that case, assumes a stratified appearance. Silver lodes are usually intimately connected with intrusive dykes of porphyry and diorite. Of this portion of South America, Bolivia, Peru, and Chile contain most of the productive silver lodes, which greatly resemble each other in characters and mode of occurrence. The famous Potosi Mines are in Bolivia (formerly Upper Peru), and the not less important mines of Cerro de Pasco are in Peru, where also in the provinces of Pataz, Huamachuco, Caxamarca, and Chota important silver mining districts exist. In Chile the silver mines are found in a narrow belt extending about 150 leagues from N. to S., which commences in the vicinity of St. Iago and ends close to Copiapó. The richest lodes occur between this city and the village of Coquimbo. R. W. Raymond estimated the total silver production of Central and South America in 1873 at $8,000,000, only an insignificant portion of which was derived from the former. The silver is met with in these lodes in the native state, in that of chloride, chloro-bromide, and iodide, and in that of simple and complex sulphides. In Chile native silver is often associated with arsenides and arseniates of cobalt and copper; and the amalgam (arquerite) has also been raised in large quantity. Proustite is nearly always found accompanied by metallic arsenic. The rich silver lodes of Caracoles, Chañarcillo, and La Florida, which contain silver chiefly as chloride, are not auriferous; whereas other lodes containing sulphides usually are so.

The silver ores are generally accompanied by sulphides of other metals and by quartz. According to Domeyko, a variety of pearl-spar, ankerite, occurs in nearly all the silver lodes of Chile, but the gangue of the rich silver lodes of the districts of Copiapó and Coquimbo is chiefly sulphate of baryta, the strings of which serve as a guide to the miners in their search for new productive lodes.

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[*] The works which have been consulted in preparing this article are the following:—Mier's Travels in Peru and La Plata; London, 1826. vol. 2. pp. 434 et seq. Travels in Peru, by Dr. J. J. von Tschudi, translated by T. Ross; London, 1847. pp. 327 et seq. Domeyko: Ann. des Mines, tom. 9. 1846. pp. 33 et seq. Domeyko: Comptes Rendus, 1842. pp. 560 et seq. Domeyko: Tratado de Ensayes; Paris and Mexico, 1876. pp. 302 et seq. El departamento de Ancachs y sus riquezas minerales, por A. Raimondi; Lima-Peru, 1873. pp. 306 et seq. Forbes: On the Geology of Bolivia and Southern Peru; Quarterly Journal of the Geological Society of London, vol. 17. 1861. Richter and Hübner: Berg- u. Hüttenmännische Mittheilungen über Mexico und einen Theil von Südamerica; Preuss. Zeitschrift, 1876. pp. 226 et seq.

Patio Process as conducted at Potosi and elsewhere in Bolivia.

The following information has been derived from various sources mentioned in the foot-note.[9] In the mountain of Potosi, which is situated close to the city of that name, and rises to a height of about 16,000 feet above the sea-level, there are numerous lodes containing iron- and copper-pyrites and silver ores, their gangue being chiefly quartz. A smaller mountain in the neighbourhood of the city is rich in lodes yielding argentiferous galena. The country-rock of all these lodes is Jurassic limestone, frequently intersected by decomposed granite. Before the introduction of the Patio process in 1571, all the ores were smelted; but since that time smelting has been abandoned on account of the great loss of silver in dressing the ores and the costliness of fuel. From the beginning of the present century to 1845, the average annual production of the Potosi Mines has fallen from 150,000 to 54,000 lbs. troy of silver, which is attributed to the decrease in the richness of the ores as the mines became deeper, to the high price of mercury, and to the bad system of working the mines. The average yield of silver from the ores, according to Humboldt, had fallen from 4·5% in 1574 to 0·04% at the beginning of the present century; and the average price of mercury, which during the Spanish dominion was 365 francs per Spanish quintal (101·442 lbs. a.v.d.), had risen in 1845 to 825 francs. With cheap mercury, ores yielding only 0·04% of silver could still be profitably treated; but in 1845 Lemuhot states that, owing to the improvements made in the Patio process at Potosi, notwithstanding the greatly increased cost of mercury, ores yielding 0·097% and even less of silver could be profitably amalgamated.

The silver ores are divided into two classes:—

I. *Pacos*, which are earthy in appearance and contain the silver in the metallic state or combined with chlorine, bromine, or iodine; if the *pacos* are accompanied by iron- or copper-pyrites, they are termed *mulattos*. (The composition of these ores is stated at p. 191 antea.)

II. *Negrillos*, which are all more or less metallic in lustre and contain the silver either as simple or complex sulphides, accompanied by sulphides of other metals. Before amalgamation, these ores, as well as the *mulattos*, if they contain a considerable amount of iron- and copper-pyrites, have to be roasted.

The ore is reduced to powder either by stamps, in a kind of *arrastre*, or by *trapiches* (edge-stone mills), the motive power being water. The *maray* method, previously described at p. 563, is still employed by the Indians for grinding silver ores. According to its nature, the ground ore is either roasted or passed direct to the *patio*, which in Bolivia is called *buytron*.[1] By a previous amalgamation of a small

[9] Procédés d'amalgamation des minérais d'argent à Potosi, par M. L. Lemuhot; Ann. d. Mines, 1858. pp. 447 et seq. Humboldt, Nouvelle Espagne; Paris, 1811. vol. 2. p. 373. Mém. Nat. Sciences; Lima, 1827 and 1828. pp. 15 et seq.

[1] Roasting is effected in reverberatory furnaces, and a charge usually of 10 quintals, with the addition of 8 lbs. of salt, is worked off in 8 hours, the fuel being dried sheeps' dung (*taquia*). See also p. 654.

quantity of the ore under treatment, the necessary quantities of *magistral*, salt, and mercury are ascertained. The presence of chloride, chloro-bromide, and iodide of silver in the ore is indicated by the mercury becoming covered with an ashy grey powder, and necessitates the use of lead- or tin-amalgam in amalgamation on the large scale. Tin-amalgam containing 5% of tin is usually employed, and is easily prepared by adding to molten tin, with continual stirring, the requisite quantity of mercury. The effect of 3 parts by weight of lead is considered as equivalent to that of 1 part of tin. The amalgamation heaps or *cuerpos*, as they are termed in Bolivia, are usually of small size, and vary from 25 *arrobas* for richer ores to one *cajon* (50 quintals = 5072 lbs. a.v.d.) for the poorer ores. The whole of the *magistral* and salt is generally added at the beginning; but the mercury and tin-amalgam are added in successive portions. In other respects the mode of amalgamating does not differ from that practised in Mexico. According to the size of the *cuerpos* and the nature of the ore, amalgamation is completed in from 8 to 12 days. In Bolivia it was customary to effect the *repasos* by men, but in 1831 Don Innocente Telles constructed a machine for this purpose, which consists of a large shallow tub, having in the centre a vertical shaft moved by a horizontal water-wheel. A horizontal arm passes through the upper portion of the shaft, and carries on each side 3 loose wheels of the same diameter, but of different widths. This contrivance ensures a proper mixing of the whole of the *cuerpo*. Washing is effected by agitating the amalgamated ore with water in a circular pit, and letting the muddy liquid run into a system of inclined channels, covered on the bottom with skins. The amalgam deposited on the skins is removed by scraping. This primitive method of washing has at most works now been replaced by a more satisfactory one, like those in use at some localities in Mexico. The average loss of mercury in the treatment of Bolivian ores, which used to be 1 lb. per mark of silver extracted, has been reduced by the use of tin-amalgam and greater care in the manipulations by one-half, *i.e.* 1 mark of mercury being lost for each mark of silver extracted.

Patio Amalgamation in the Department of Ancachs, Peru.

For the following description of the process of extracting silver by amalgamation from argentiferous copper ores, as generally practised in the Department of Ancachs, Peru, I am indebted to my friend Mr. William Ratcliffe, who was for several years engaged as an assayer in Peru, and who had previously studied in the Metallurgical Laboratory of the Royal School of Mines in London. It is founded on his own personal observation, and was communicated to me in 1867.

The ores which he has seen used in this process are of two kinds, namely, *metales calidos* (hot ores) and *metales frios* (cold ores.)[2] The

[2] See note on this subject at p. 222 antea.

first kind consists mostly of various sorts of *paco*, a term applied by Peruvian miners to silver ores other than native silver, argentite, and complex sulphides and arsenides. They often contain chloride of silver, and sometimes a little silver in the metallic state; but probably most of the silver in them is in combination with sulphur. They are generally largely composed of hydrated ferric oxide and basic ferric sulphates, with every variety of earthy gangue. Mr. Ratcliffe has sometimes found them to contain arsenic in an oxidized state, combined with ferric oxide, and once he met with a *paco* ore mainly composed of antimony ochre. Ferrous sulphate, in small granular crystals, is occasionally, and malachite very frequently, present in these ores. Some of the pacos are very similar to the ferruginous gossans of Cornwall. The other kind of ores or *metales fries* consist, according to Mr. Ratcliffe, of antimonial *fahlerz*, with a greater or less intermixture of blende, galena, and iron- and copper-pyrites, the matrix being quartz: they are sometimes very rich in silver.

Mr. Ratcliffe thinks that in most cases the *pacos* form the outcrop of veins, and have resulted from the oxidation and hydration of the [illegible]. Löllingite, $FeAs_2 = FeAs^2$ [idem], is, he says, common in Peru, and seems to weather very readily, and thus to produce a kind of gossan of frequent occurrence.

There is another kind of ore in which the silver exists either native or in the state of chloride; but he has not seen the process of treating them. Tetrahedrite and pyrargyrite have also been found in crystalline specimens in certain mines, yet only in pockets, and not forming the chief metalliferous constituents of the veins.

AMALGAMATION OF THE "METALES FRIOS."

These ores are amalgamated in the raw state. The ore is ground in an edge-runner, generally of granite, working on a bed of the same material, and moved by a horizontal water-wheel. The bed-stone is surrounded by a low wall so as to form a shallow basin, about 6′ [illegible] wide, in which a small stream of water constantly runs, and flows out through a notch in the rim of the wall, ore being thrown in as required. Ore is thrown into the mill from time to time, and as fast as it becomes finely ground it is carried off by the escaping current of water into an adjacent pool called a *cerco*, which is a circular [illegible] paved with stones and cement, and bounded by a wall [illegible] high. In the centre there is a broad short pillar, on which stands the post on which drives round the mules employed in working the mill. The ground ore settles down in the *cerco*, the water running away at an opening left for that purpose. When a [illegible] has accumulated, say from 50 to 100 tons, according to [illegible] the water which remains is allowed to evaporate [illegible] reduced the consistence of thick mud. After the [illegible] by mules until it has become uniform through- [illegible] salt is added in the amount of about 5% of the weight [illegible] treading is repeated and continued until thorough

in.

On the following day the *magistral*, or roasted copper-pyrites, is added, the quantity being regulated by the experience of the workman; and as an excess of it would occasion an undue waste of mercury, it is very important not to add too much. The mass is again trodden, after which the mercury is distributed over the whole surface by squeezing it from a leather or canvas bag, the quantity of mercury used being about 3 lbs. to every mark of silver supposed to exist in the ore. As soon as the mercury has been added the mules are again set to work, and the treading is repeated every day or two days until the amalgamation is completed, which occurs after the lapse of from 10 to 30 days, according to the quality of the ore and the state of the weather. From time to time a sample of the mass is washed in a *puruña*, or flat dish made of unglazed red earthenware or of wood, in order to ascertain how the process is going on; and in the management of the process there is no operation which requires so much experience. Nothing but actual practice can enable anyone to form a correct judgment on the subject, from the varying appearances of the amalgam after the associated earthy matter has been washed away from it; and there are no other indications to guide the amalgamator. By these trials it may be known whether the action of the *magistral* is what it should be: if too rapid, the addition of *lime* or *wood-ashes* is required; and if too slow, more *magistral*.

When the amalgamation is completed, the mules are again set to work, while, at the same time, a proper stream of water is allowed to run through the *cerco* until the greater part of the earthy matter has been removed. What remains is then collected and finally washed in stone cisterns, with a constant stream of water flowing through them, until the amalgam is sufficiently clean. The amalgam, after having been dried with a sponge or cloth, is filtered in a conical bag of strong linen cloth, expulsion of the mercury being aided by careful pressure with the hands. The hard amalgam, or *pella*, is heated in a pear-shaped vessel, made of unglazed coarse red earthenware, with a long neck and narrow mouth, to which a pipe is attached to conduct the condensed mercury into a bucket of water. A fire, generally of charcoal, is made round the vessel, which is set in a kind of hearth, and kept at a red-heat until no more mercury distils over; but the temperature is never allowed to rise so high as to melt the silver. After this operation the earthen vessel is broken, and the silver extracted as a spongy mass, which, under the name of *plata piña*, is sold to merchants who make a business of buying it and melting it into bars. This is generally done in the ordinary iron quicksilver bottles, cut off at the shoulder, and heated in a blacksmith's forge.

The quantity of mercury which is *consumed*, or lost partly by chemical action and partly as amalgam mechanically diffused through the *relaves* or residues, is generally from 12 to 16 ozs. to 1 mark of silver obtained.

AMALGAMATION OF THE "METALES FRIOS."

The second kind of ores, or the *metales frios*, cannot be profitably worked without having been previously roasted, in which operation a large quantity of the antimony is evolved in the form of dense white smoke. The ore is ground dry, and passed through a sieve of 60 holes to the linear inch. The meal is roasted in a flat-bedded reverberatory furnace, having a low arch, the flame generally entering at the four corners, and escaping through an opening in the centre of the arch in its course to the chimney. The fuel used is *taquia*, or dry sheeps' dung.

At the Hacienda de Santa Rosa, Recuay, the beds of these furnaces are 19′ by 9′, and in each furnace can be roasted 8 cwts. of ground ore per day of 24 hours, with a consumption of from 20 to 24 cwts. of *taquia*. The roasting lasts from 8 to 12 hours, according to the quality of the ore; when it is completed, the ore is withdrawn from the furnace and cooled with water. It is then taken to a paved yard, and piled in heaps of about 2 cwts. each, to which the proper proportion of salt is added (about 5% of the weight of the ore), and water to make the whole of a suitable consistence.

Magistral is not added, because, in the roasting, sufficient sulphate of copper is formed from the copper sulphides always present in the ores. The mass is mixed by men, who tread it barefoot, and turn it over repeatedly with shovels. Next day the mercury is added, and the treading repeated. Amalgamation is completed in from 10 to 15 days, and its progress is ascertained in the manner stated in the description of the amalgamation of the *metales calidos*. When the operation is ended, the mass is stirred with water in a stone cistern, by men who trample upon it until the earthy matter is washed away, a current of water being made to flow through the cistern all the while. The amalgam is treated like that from the first kind of ores.

PATIO PROCESS AS PRACTISED AT THE CERRO DE PASCO MINES OF PERU.

The village of Pasco is situated 13,673 feet above sea-level, on the ridge of Yauricocha, 58 leagues from Lima and 20 leagues from the town of Tarma, on the high road to Xauxa. Two remarkable silver lodes occur close to the village in the Cerro de Pasco. The first, called Veta de Colquirirca, runs nearly from N. to S., and has been traced 9600 feet in length and 412 feet in breadth; the second, known as Veta de Pariarirca, trends from E.S.E. to W.N.W., and intersects the first lode, it is supposed, exactly under the market-place of the village. The known extent of the second lode is 6400 feet in length and 380 feet in breadth. From these large lodes numberless smaller ones branch off in various directions, thus forming, it may be conjectured, a network of silver ores spreading beneath the surface of the earth.[3]

[3] Travels in Peru, by Dr. J. J. von Tschudi, translated by T. Ross. London, 1847. p. 330.

The Cerro de Pasco Mines, which were accidentally discovered in 1630, have yielded from that time up to the present, according to Mr. Castlenau, an annual average of $2,170,000 worth of silver.

Domeyko states that the pockets of ore found in these lodes, called *cascajo*, are of an enormous size, and consist of a kind of quartz mixed with a yellow ochreous clay, which contains finely disseminated native silver in such small quantity that the average yield of these ores scarcely reaches 0·19% of silver. The *pacos* of these mines, the average yield of which does not surpass that of the *cascajo*, appear to contain, besides native silver, horn-silver, argentite, and proustite. None of these ores require previous roasting, and their treatment by the Patio process is the same as that previously described and in use in the department of Ancachs.[4]

Patio Process as practised in Chile.[5]

The percentage of silver in the ores treated by amalgamation in Chile varies considerably. In Copiapó ores containing less than 0·3% of silver are seldom, and then only in small quantities, subjected to amalgamation; the ground ores of Arqueros, containing the silver chiefly in the state of amalgam, usually yield from 1·0% to 1·2%,[6] the grey-copper ores of Machetillo 0·8%, and the copper-pyrites ores of Catemo and San Pedro Nolasco from 0·5% to 0·8% of silver.

According to Domeyko, the Patio process is now (1876) employed, to a limited extent only, for the treatment of ores containing the silver either as sulphide, arsenide, antimonide, or argentiferous copper sulphides (*metales frios*). Usually these ores are subjected to a previous roasting, with or without the addition of salt. But as these methods, as well as those which have been adopted in other parts of America, for the treatment of similar ores, entail either great loss of metal or considerable delays, most of the *metales frios* are at present exported in their crude state, or after their conversion into regulus by smelting them with the addition of copper or lead ores.[7]

Ores containing the silver chiefly in the metallic state, or as native amalgam, such as those of Arqueros, are amalgamated in heaps, with the addition of salt and mercury (without any *magistral*). Towards the end of the process a small quantity of *pir*, i.e. lead-amalgam in the state of powder, and composed of equal parts of lead and mercury, is sometimes added to reduce the little chloride of silver which the ore may contain, or which may be formed during the process. The process lasts from 6 to 8 days, and the loss of mercury does not exceed 4 ozs. per mark of silver produced.

Ores consisting chiefly of horn-silver, chlorobromide and iodide of silver (*metales calidos*), are treated by the Tina process (*v.* p. 567

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[4] Tratado de ensayes, por Ignacio Domeyko. Paris and Mexico, 1876. p. 302.

[5] Domeyko, op. cit. pp. 327 et seq.

[6] The *relaves* from these ores are said to retain from 0·05% to 0·055% of silver; but if the ores under treatment contain also sulphides of silver, the percentage of the *relaves* reaches sometimes 0·15%.

[7] Evidently Domeyko entirely ignores Kröhnke's process of amalgamation to be hereafter described.

antea), with a loss of mercury not exceeding 2 or 3 ozs. for every mark of silver extracted.

The *plata piña* of Chile retains from 3% to 4% of mercury, also some lead if that metal has been used in the amalgamation process, and sometimes traces of copper. Its fineness varies, therefore, from 960 to 970, and rarely reaches 980.

Theory of the Patio Process.

The consideration of the Theory of the Patio Process will appear at the beginning of the next volume on the Metallurgy of Silver and Gold, much of which is already in type. A fresh investigation concerning the chemical réactions which occur in this process has recently been conducted in the Author's laboratory, and, although it has occupied many months, it is not yet completed.

CAZO OR CALDRON PROCESS.

The priest Albaro Alonso Barba claims to have invented this process in 1609, when residing at the town of Tarabuco, in the province of Charcas, in what was then Upper Peru, but is now Bolivia. He has given the following account of the manner in which the invention originated:[1]—"Wishing to try an experiment on a method of fixing quicksilver in an iron vessel, of which I had read, and not having such a vessel, I used one of copper. But not succeeding in the operation, I added finely-ground silver ore to the quicksilver, with the notion that the mineral virtue of this stone might, by the heat and moisture of coction, further my object. In a short time I extracted a quantity of silver amalgam and silver, which at first much surprised me; but my astonishment ceased when I found that the silver collected by the quicksilver had come from the ore and not from quicksilver transmuted. I was highly satisfied with this my new and short method of extracting (*beneficiar*) metals, which, after reflection and constant experimenting during many years, I have since improved. I have made it publicly known, and have not kept either it or other secrets to myself. In 1615, having the cure of Tiaguanaco, in the province of Pacages, I continued to carry on this process more at leisure (*mas comodidad*); and since 1617, while officiating in the province of Lipas, more frequently and with greater profit. During this period, some persons claiming for themselves the credit due to others tried to obtain large premiums in different localities for the introduction of this new process of extraction; but their own blunders and the experience of others have proved that they were not the inventors, and did not understand the principles of the process. No one taught it to me, and I know no author, either ancient or modern, who has mentioned it. On these grounds the Royal Court (*Real Audiencia*) of La Plata granted me an exclusive right, forbidding all other persons whomsoever to use the process

[1] Arte de los Metales, 1640. antea cit. Libro iii. Also the French translation, 1752. antea cit. The English translation of Barba's treatise, by the Earl of Sandwich, does not extend beyond the second chapter.

without my consent. With some special reservations, I have since permitted every one to practise it, without any profit to myself."

Barba directs that the caldron should be made wholly of well-refined copper; for, if it contain any admixture of lead, tin, gold, or silver, the mercury would perforate it and pass through the bottom, from the facility with which it unites with those metals. The size of these vessels must depend upon the quantity of material treated at a time; their capacity varies from 175 to 350 gallons. The bottom is to be beaten out of a single piece of copper into the form of a frying pan, half a finger thick and from 6 to 8 fingers deep. The upper part of the caldron is made of sheet copper, tightly riveted to the bottom, and about half as thick as the latter, or a little less. In Barba's original treatise there is a rude woodcut of the caldron, in which it is shown of the shape of an inverted truncated cone, the diameter at the top being somewhat more than twice that at the bottom, and not quite so deep in the middle as wide at the top. Round the top is fixed a hoop of copper or iron, provided with two strong upright and opposite handles, to receive the ends of a bar placed across, which may be firmly fastened by wedges. Within the caldron is fixed a stirrer, which consists of a vertical shaft with four similar and equal arms at right angles to the axis, to each of which is attached a series of vertical bars, decreasing in length towards the sides. In the top of the shaft is a spindle which passes through the transverse bar, and at the bottom a pivot which works in a bearing of bronze in a bar of copper extending across the bottom of the caldron. The stirrer is made light, and, except in the parts above specified, wholly of wood; and rotation is imparted to it by means of a handle fitted on the top of the shaft. The construction of the stirrer is similar to that of the washing machine shown in fig. 93. The bottom of the caldron is set in a round hole in the top of a furnace built of unbaked bricks; and Barba has described and figured a furnace with four of these caldrons in line on the top, the fireplace being in the centre and a low chimney at each end: wood was the fuel used.

The ore must be very finely ground and sifted, and if, on afterwards rubbing it between the fingers, any grittiness should be perceived, it must be stirred up with water in a vessel, and then left at rest for a few moments until the coarse particles have subsided. The supernatant muddy liquor is now put into the caldron, previously charged with mercury proportionate to the richness of the ore, but never less than suffices to cover the bottom, and with some clear water. The water is made to boil and kept constantly boiling, the stirrer being gradually brought into action. Loss by evaporation is supplied by the continual flowing into the caldron of water so hot as not to check ebullition. With too much water the operation is prolonged, and with too little the mixture is so thick as to prevent its rapid rising and falling during boiling.

From time to time some of the mixture is taken from the bottom with a ladle, or, if it is wished, some of the amalgam, in order to ascertain how the process has gone on, and if it is necessary to

add more mercury. The surest way of finding whether the ore has yielded the whole of its silver is to add a little fresh mercury to some of the washed ore in a bowl, shake the latter two or three times, and observe whether any silver is taken up by the mercury or not. If not, the boiling is stopped, the stirring apparatus removed from the caldron, the muddy liquor laded out and left at rest, in order that any suspended amalgam may subside. The coarser part of the ore which has settled down upon the mercury is also removed, after which it is assayed, and, if necessary, reground and boiled again in the caldron.

The silver is extracted from the amalgam in the usual manner, as previously described.

Barba asserts that every kind of silver ore in its crude state may be directly subjected to his process; but that certain kinds, without the addition of particular substances, would require a longer time. The ores which yield their silver most quickly and easily, and may be directly treated by this process, are called *pacos*, *tacana*, *plomo*, and *plata blanca* (white silver). From the description given by Barba of these ores, their nature cannot be inferred with certainty. The first kind had no metallic lustre, and seems to have been gozzan containing chloride or chloro-bromide of silver, with, it may be, metallic silver; the second was a rich ore, without metallic lustre, generally black, but occasionally grey and ash-coloured, characters which are not sufficient to indicate its nature; the third was always rich in silver, could not be ground when in too large lumps, did not combine easily with mercury in the Patio process, and was black, grey, ash-coloured, green, white, or orange, from which description it may be inferred that several species were included under this name, one of them being argentite and another chloro-bromide of silver; the fourth kind was probably native silver more or less massive.

Although Barba asserts that all the ores of silver above mentioned can be treated directly by his process, as conducted in the manner described, yet it is well to calcine them previously, especially the *plomos*, "because it cleans and purifies them, whereby they better yield up their silver." That this effect should result from the roasting of argentite is intelligible, but not in the case of ores in which the silver exists wholly or mainly in combination with chlorine or bromine.

The class of ores named *negrillos* (diminutive of *negro* in Spanish), which seem to have included all complex sulphuretted ores, not excepting red silver ores and such as are plumbiferous, are best smelted; but if treated by the Caldron process, it is necessary to calcine them previously, until they change colour and lose their lustre, or, instead of calcination, to add certain substances during the boiling, namely, "*copaquiras* (cupric sulphate), or *caparrosa* (ferrous sulphate), *millo*, or alum, salt, or things which contain it such as urine, or strong leys."[2]

[2] The original Spanish is as follows: "copaquiras, o caparrosa, millo, o alumbre, sal, o cosas que la contienen, como son origines, o legias fuertes." Lib. iii. cap. 5. *Millo* elsewhere in Barba's treatise is said to be a kind of salt.

In the course of working, a little of the copper of the caldron is always consumed; and the bottom is most acted upon at the circumference at the level of the surface of the mercury. In the latter case erosion, which Barba attributes to the mechanical action of the mercury caused by the boiling, may be prevented by fixing round that part of the bottom a band of copper, which may be replaced at a small cost when it has worn away. The caldron is quickly corroded when such substances as those previously specified, namely, copperas, alum, etc., are used in the process, as in the case of operating on *negrillos* ores in their crude state; a practice which Barba does not recommend, and which, he says, he merely mentions in order to make known the possibility of successfully treating those ores by his process without having first calcined them. He adds that although much might be gained by this method of proceeding, yet, owing to the corrosive action of the substances added upon the copper, it is advisable to avoid using them by previously calcining the *negrillos* ores.

Barba compares the Patio process with his own, and maintains that the latter is superior to the former in the following respects:— Greater yield of silver to the amount of $\frac{1}{6}$; no loss of silver such as occurs in the Patio process from the argentiferous mercury left in the residues; less loss of mercury; less consumption of salt; much shorter duration, a month being required for the Patio process, and only 24 hours for his own; and greater profit. It should be particularly noted that whilst previously Barba only mentions the use of salt in the Caldron process in exceptional cases, he seems here to intimate that it was always used in that process. The necessity for wood as fuel cannot, he says, be urged as an objection, because it is always to be had in Peru at a sufficiently low price.

Cazo or Caldron Process as practised in Mexico.

This process has long been practised in Mexico, but not so generally as in South America, which, as Duport suggests, may be explained by the circumstance that ores suitable for it, namely, such as contain haloid salts of silver in large relative proportion, are less abundant in the former than in the latter part of the American continent.[3] With a few rare exceptions, the ores subjected to the Cazo process are nearly always *colorados*. They are crushed and ground in the *arrastre*, but less finely than for Patio amalgamation, because the ground ore has to be concentrated by washing, and considerable loss of silver might occur if the grinding were carried too far. The ore is washed on a *planilla*, and is thereby reduced to about 2%[4] of its original weight.

The *planilla* here referred to is a concave inclined plane, with a

[3] Op. cit. pp. 144 et seq. The description here given is founded on information derived from Duport's treatise and Laur's paper (Ann. des Mines, 1871. 20), which have been so often quoted in the preceding pages.

[4] At p. 292 Duport states from 1% to 2%.

trough at the lower end. Duport states that at Catorce the washing is conducted with rare dexterity; the heavy particles or *schlich* seldom extend beyond the middle of the plane from the top, while the light particles or slime accumulate on the lower portion, and there form a layer of from about 4 to 8 inches thick. When the dresser considers the ore to be sufficiently concentrated, a slice is taken from the whole width of the layer of slime and vanned, when, if the least trace of "green silver" is perceived, the slime is thrown back on the *schlich* and the same operation repeated until no indication of the presence of silver is afforded by vanning. The washing of the *schlich* is continued, and, after a last examination, all the slime is conveyed into a reservoir previously containing the mud separated by washing from the ore after leaving the *arrastre*.

The *cazo* or caldron formerly in use was of a very primitive character, and similar to that of Barba, though not exactly the same, as Duport supposed it to be. It is a round vat, of which the bottom is made of copper, and the upper part of wooden staves or of stone; it is about 0·7 metre in diameter at the bottom and 1·0 at the top, and about 0·5 deep. The copper bottom is turned up at the edges, as shown in section in fig. 95, *a*: it consists of a single casting, and varies from 0·03 to 0·08 metre in thickness, according to the degree of wear to which it has been subjected. The staves forming the upper part are grooved at the base and rest on the rim of the copper bottom. All joints are luted with clay, with which also the outside, except round the top to the depth of about 0·13 metre, is pretty thickly coated, this coating being supported by a surrounding wall of sun-dried bricks (*adobes*). The copper bottom, of which the circumference rests on the same wall, forms the roof of a fireplace without either grate or chimney, and with a single opening for the introduction of fuel (wood), the escape of smoke, and the removal of ashes. The foregoing description will be rendered more intelligible by an inspection of fig. 95, which represents an improved and much larger kind of *cazo*, only the reader must conceive the grate *g* to be omitted. Just above the rim of the copper bottom, on one side, a pipe is inserted, which slopes downwards and outwards, and by which all the muddy liquor above the point of insertion may, after the completion of an operation, be made to flow into an adjoining tank.

The fire having been lighted, as much water is poured into the *cazo* as will form a very liquid mud with the charge of ore, after which the ore is immediately added. As soon as the liquor begins to boil and becomes thoroughly agitated by the bubbling, common salt is thrown into it in quantity varying from 10% to 20% of the weight of the ore. The salt must not be added before the liquor boils, for, otherwise, it would subside and form with the ore a solid mass, adherent to the copper bottom, from which it could not be separated without emptying the *cazo*. When once the salt has been put in, a man incessantly stirs the liquor with a club-shaped piece of wood, so as to produce continual friction upon the copper bottom. Charging

with mercury now begins. The quantity is proportionate to the richness of the ore, but in the whole operation it ought not to exceed twice the weight of the silver. At first a quarter of the total mercury is poured in, and an hour afterwards an assay is made of a portion of the heaviest part of the ore and of the amalgam, scraped off the copper bottom by means of a curved horn fixed to the end of a long handle. This portion is washed in a bowl so as to remove the lightest particles and uncover the amalgam, which, if the operation is going on well, appears in the form of very fine grains of a light leaden grey colour. This kind of amalgam is called "dust" (*polveo*), and experience has shown that it consists of about 2 parts of mercury and 1 of silver by weight. From time to time fresh quantities of mercury are added, and the assays repeated until it is perceived that the amalgam varies as to its hardness and state of division. The operation is now regarded as ended; but before it is stopped another assay is made, called the "crude test" (*prueva en crudo*), in the following manner. A certain quantity of the amalgam having been washed in a horn spoon, so as to remove the whole of the ore, a little mercury is added to the former and the whole rubbed with the fingers, when, if the liquid mercury added is observed to solidify, more mercury is poured into the *cazo* and the operation continued; because such a result of the trial indicates that the proportion of mercury is still insufficient for the extraction of the silver. But when the contrary indication occurs, the liquor in the *cazo* is laded with buckets into a tank, from which it is put back into the *cazo* for the next operation.[5] The solid deposit of ore containing the amalgam is laded out by means of wooden bowls, and forthwith washed in the large wooden dishes, after the addition of about as much mercury as has been used in the *cazo*, rather less than more, the object being to form a less dry amalgam, so that it may collect into a mass and be no longer liable to be carried away by the water along with the earthy residue. The proper consistency to be given to the amalgam to prevent loss in washing is an important point: in the state of *polveo* its division is such that a portion of it might easily be removed by the water; and if, on the contrary, the mercury be in excess and the amalgam very liquid, particles of it might be projected beyond the rim of the dish, owing to the force of the shocks which are required to free it from the last fragments of the gangue.

Duport, in 1843, states that about 50 years previously the *cazo* of the kind above described was replaced by one of much larger dimensions, designated in Spanish *fondon*, which is constructed on the principle of an *arrastre*. Such an apparatus is represented in fig. 95, which is copied from an engraving accompanying Laur's description of the Cazo process.[6]

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[5] In the engraving which accompanies this description by Duport a pipe is shown by which the liquor may be drawn off a little above the bottom; and an account of the same arrangement appears in an earlier part of his description of which the translation is here given.

[6] Annales des Mines, 1871. 6th series, 20. pp. 216 et seq.

Such a *fondon* as is here represented costs, according to Laur, $1579, and may last 10 years. The value of the copper amounts to 76% of the total cost.

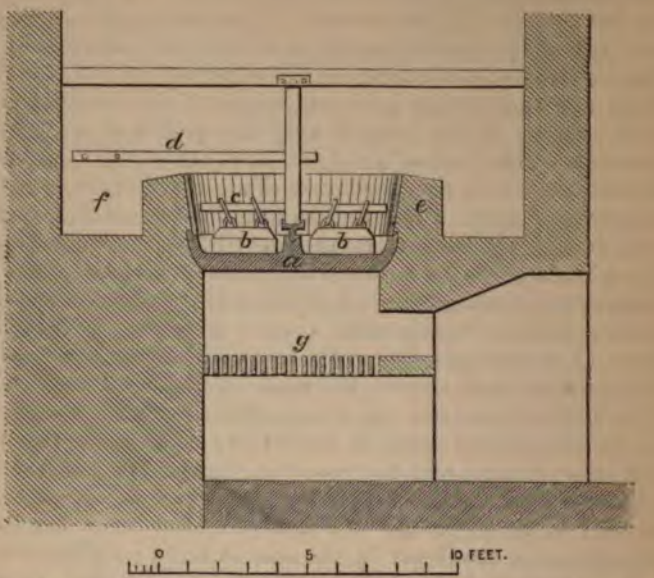

Fig. 95. Vertical section of the *fondon* through the centre. The *fondon* is circular, like the *cazo* previously described; the bottom is made of copper, and the upper part of wooden staves bound with strong hoops of iron.

a. Bottom made of impure copper and cast in one piece. It is 1·8 metre in diameter, 0·18 in depth, and from 0·18 to 0·20 in thickness. In the description of a *fondon* by Duport, the diameter of the copper bottom is said to vary from 1·75 metre to 2·25. In the centre is a projecting piece, which receives a bronze pivot fixed to the lower end of a vertical shaft of wood. In Laur's description of the process a hole in the bottom is mentioned, by removing a plug or bung from which the muddy liquor may be drawn off, though no such hole is shown in his engraving: it is situate, according to Duport, in the side of the *cazo* near, but above, the copper bottom, and not in the latter, as might be inferred from Laur's description.

b, b. Blocks or *voladoras* of cast copper attached to the lower arms, *c*, of the shaft, each block weighing 138 kilog.

d. Arm by which the shaft is made to rotate by a single mule.

e. Surrounding wall of solid earth.

f. Mule-walk.

g. Fire-place, with a grate. Inferior wood is used for fuel, such as the trunks of palm-trees and stumps of American aloes (*Agave Americana*). No mention is made of any flue, so that the smoke must escape from the opening through which the fuel is introduced. In the description of a *fondon* by Duport it is stated that there is no fire-grate, and that the consumption of fuel is very wasteful.

The following description of the mode of conducting the process in the *fondon* is given by Laur. The charge for a *fondon*, of the dimensions shown in the woodcut, is 48 *arrobas* (1200 lbs. Spanish) of rich ore and from $2\frac{1}{2}$ to 3 *arrobas* of very fine slimes from unwashed ores. The quantity of salt, described as ground sea-salt, is stated to be about 10% of the weight of the ore; but the total quantity of mercury is not precisely specified, all that is mentioned on this point being, that the first dose of mercury is equal to half the weight of the silver, the second dose is the same as the first, and that afterwards more continues to be added until a soft amalgam, moistened with mercury in excess, is obtained.

After the ore has been introduced, sufficient water is poured in to

form with it a thin muddy liquor. The fire is urged vigorously, and the mule set in action. After the lapse of 2 hours, when the liquor should be in full ebullition, the whole of the salt and the first dose of mercury are added, and the pace of the mule is accelerated to the extent of about 10 turns per minute. An hour after the addition of the mercury, an assay is made exactly in the same manner as described by Duport; and in this, as well as other parts of his description, Laur has evidently quoted from Duport's treatise, though without acknowledgment. The amalgam, which is composed of 2 parts of mercury and 1 of silver, should, according to Laur, now appear in the form of "crystalline sand of a very light ash-grey colour" (*sable cristallin gris cendré très-clair*). A second dose of mercury, of the same weight as the first, is now put into the *fondon*, ebullition being kept up and the mule driven at the same pace as previously. An hour afterwards, a fresh assay is made, when the amalgam should be found to be in the dry state. Fresh mercury is added until the amalgam becomes soft and moistened with mercury in excess, and continues so even after having remained for half an hour longer in the *fondon*. The operation is then regarded as ended, though a further assay (*prueva en crudo*) is made in the manner stated in the foregoing description by Duport. Laur, however, adds that after having poured off the amalgam in this last assay, the residue of ore in the dish should be strongly rubbed against its sides in order to see whether it contains any particles of *plata verde* (chloride or bromide of silver); and if it should, the operation in the *fondon* should be prolonged, but without any further addition of mercury. When the operation is completed, which generally occurs after the lapse of 6 hours, the muddy liquor is drawn off through the hole in the side near the bottom into tanks, and the heavy deposit on the bottom is laded out. This deposit usually consists of oxidized ores of lead, iron, etc., of a very small quantity of sulphides containing silver, etc., and of silver amalgam in powder. It is washed in large wooden dishes, with the addition of a quantity of fresh mercury equal in weight to the total of that previously added. The amalgam, thus freed from intermixed impurities, is treated in the usual manner: the resulting silver generally contains a little copper, which is separated by refining with lead.

Laur asserts that the reducing action upon the ore is proportionate to the quantity of salt used; that for the richest ores it ought never to exceed 25% of their weight, and that it is accelerated by increasing the speed of rotation of the copper blocks. With one mule, however, it is hardly possible to obtain more than 10 turns a minute.

In conducting this process of hot amalgamation, the most important point, according to Duport, is to prevent the mercury or silver amalgam from adhering to the surface of the copper. In repeated trials he observed, that so long as the proportions of mercury and reduced silver were as $Hg^2 : Ag$ [Hg : Ag], *i.e.* about 2 : 1 by weight, such adhesion never occurred. Even with twice that proportion of mercury, there was no inconvenience; but beyond that limit adhesion was immediately manifested, and though, subsequently,

the amalgam might, by taking up a larger quantity of silver, become very dry, yet the layer of mercury adherent to the copper was thereby rarely removed, the operation was prolonged, and, as regards the loss of mercury and the yield of silver, the results were always bad.[7] Adhesion, however, may take place when the mercury is not in excess, if the speed of rotation of the copper blocks be too slow, in which case the copper amalgamates with the mercury, and its surface becomes coated with a very thin, yet very adherent, layer of silver amalgam. This accident may easily be prevented by keeping the mule going at a pretty quick pace, and adding the mercury in very small doses; but should it occur, it can only be remedied by emptying the vessel and mechanically removing the deposit formed on the bottom. Barring this accident, the Cazo process affords regular results, nearly independently of the skill of the workmen; and, what is of great consequence to miners of limited means, yields those results in the course of a few hours.[8] The preceding remarks in this paragraph, though for the most part referring to the operation in the large vessel named *fondon*, are yet equally applicable, *mutatis mutandis*, to the primitive *cazo*.

In the Cazo process the loss of mercury is said to be purely mechanical, and, according to Duport, did not, in a long series of operations at Catorce, exceed, on the average, 2% or 3% of the quantity put into the *cazo*, or about 1½% of the total quantity, which corresponds to ⅝ oz. per mark of silver of the silver obtained.[9] The more recent statement on this subject by Laur is, that in works at Matehuala and Catorce the loss has been found to vary from 1½% to 2% of the mercury used. "The preservation of the mercury in the *cazo*," Laur maintains, "is the distinctive feature of hot amalgamation."[1]

It is asserted, both by Duport and Laur, that while, in the Cazo process, the amalgamation of native silver and of chloride, bromide, or iodide of silver is easily effected, sulphuretted compounds of silver, whether simple or complex, are not acted upon, and will, therefore, be found in the slimes from the washing of the amalgam. After an operation conducted with the greatest care, at works on the *Cerro de San Pedro Potosi* (Mexico), Laur assayed the residue and found it to contain 0·075% of silver; and at Matehuala, the ore-mud, collected as it left the *cazo* and evaporated to dryness, yielded by assay 0·125%. Duport states that the slimes separated by washing the ore on the *planilla* are generally rich enough to be subjected to the Patio process, and that they are treated by that process in admixture with the residues from the *cazo* which are not free from silver. The presence of silver in these residues is said to be owing to the fact that the ore contains compounds of that metal which are irreducible in the *cazo*, and probably also to the operation not being sufficiently complete to extract the whole of the silver susceptible of reduction. The fear of having silver amalgam or mercury adherent to the copper bottom

[7] Op. cit. p. 153.
[8] Laur, Op. cit. p. 219.
[9] Op. cit. p. 151, and p. 290.
[1] Op. cit. p. 220.

induces the workmen (*cazeadores*) often to use far less mercury than is necessary to ensure the collection of the whole of the silver that has been reduced to the metallic state, a matter of trifling inconvenience, inasmuch as it is recovered in the supplementary treatment.[2]

As it rarely happens that the ores subjected to the Cazo process are quite free from sulphuretted silver ore, the residues are reserved for treatment by the Patio process.[3] The ore-mud, after having been left to dry in the usual manner until it has acquired the proper degree of consistence, is either distributed amongst ordinary *tortas*, or made into small heaps trodden by men. From 2% to 2½% of salt is added, but no *magistral*, because it is said that the liquors from the *cazo* "hold in solution sufficient copper salts for the reactions" (Laur). Amalgamation is conducted in the usual manner; but it proceeds very slowly, and at Catorce continues during 3 months. The loss in silver is always very high, varying from 20% to 25%; and the consumption of mercury is generally from 1¼ to 1½ for 1 of silver obtained.[4]

Cost of the Cazo or Caldron Process.

According to Duport, the cost of and process is much less with the small *cazo* than the large one or *fondon;* but if this be correct, why, it may be reasonably asked, should the *fondon* ever be used? As it seems probable that a mistake has been made on this point by Duport, only a detailed statement of the costs with the *fondon* will here be presented, and the following, which is given by Laur, has been selected.

In each operation at Matehuala and Catorce, where the process is extensively carried on, the charge of ore is 48 *arrobas* (1200 lbs. Spanish), and the *fondon* used is such as has been previously described.

Cost of One Operation.

	$
Amalgamator (*cazeador*)	0·500
Fireman (*atizador*)	0·250
Palm wood	1·562
Salt, 75 lbs., at $6 per *carga* (300 lbs)	1·500
Mule, keep per day	0·187
Mercury, 2% lost, at $65 per *quintal*	0·416
Distilling off the mercury and miscellaneous expenses	0·250
	4·665

The cost of stamping and grinding is much lower than in other districts, for which Laur assigns the following reasons:—Ores intended to be washed on the *planilla* ought not to be as finely ground as those to be treated by the Patio process; and ores in which the silver exists in combination with chlorine and bromine, as is the case in the localities above mentioned, occur in marly gangues (*gangues*

[2] Duport, op. cit. p. 150. [3] Laur, op. cit. p. 220.
[4] Laur, ibid.

marneuses) which are very easily pulverized. The frangible nature of the gangues which usually accompany chloride and bromide of silver, the granular state of these mineral species which enables them to be enriched by washing, and the low cost of the Cazo process, explain why ores of this kind, containing very little silver, may be profitably worked. Thus, at the *La Luz* mine at Catorce, provided the supply of 1000 charges (*i.e.* 138 metrical tons) of ore per week may be maintained, the cost of raising and hand-picking of the ore does not exceed 4 reals per charge. The cost of carriage per charge from the mines to the amalgamation works amounts to 3 reals, and that of the metallurgical treatment, in consequence of the large production of the mines, decreases to 10 reals.

Laur asserts that 0·03935% is the lowest proportion of silver compatible with profitable treatment of the ores at Catorce by a combination of the Cazo and Patio processes; and the statement which he presents on this point is as follows, estimating the expenses in grammes of fine silver:—

Cost per Metrical Ton of original Ore (1000 Kilog.).

	Grammes.
Extracting and dressing the ore	92·59
Transport	69·44
Metallurgical treatment (Cazo and Patio process) ..	231·47
	393·50

The ores, which are first subjected to the Cazo process, yield about 400 grammes of silver per metrical ton by that treatment; an amount which, it will be perceived, is only slightly more than sufficient to cover all the costs stated in the preceding summary. The profit, consequently, is derived from the treatment of the residues, under which term are included the slimes and poor *schlich* (*les schlamms et sables pauvres*) separated from the original ores by washing on the *planilla*, and all the ore-mud from the *cazo*. These products are subjected to the Patio process, and yield from 1 to 1½ oz. per *carga* (300 lbs. Spanish). Hence the "exploitations" of chloride and bromide of silver ores at Catorce may afford a profit when they contain from 3 to 3½ ozs. of silver per *carga*, i.e. from 0·06% to 0·07%, a proportion which would generally be insufficient for quartzose lodes with ores of sulphide of silver.

Theory of the Cazo or Caldron Process.

The theory of this process is so obvious as to require only a few remarks. The reduction of the haloid salts of silver existing in the ore is mainly effected by metallic copper, and promoted by the solvent action of the boiling solution of chloride of sodium on those salts. The cupric chloride, which is at first formed, is subsequently converted into cuprous chloride by contact with the mercury and metallic copper.

APPENDIX.

NOTE ON THE OCCURRENCE OF SILVER ORES IN NEW SOUTH WALES, BY PROFESSOR LIVERSIDGE, PROFESSOR OF GEOLOGY AND MINERALOGY IN THE UNIVERSITY OF SYDNEY.

25, Savile Row, W.
March 24, 1879.

MY DEAR DOCTOR,

I am sorry to say that I have not been able to find any reports upon the silver deposits recently found in New South Wales, *i.e.* none by trained geologists or mineralogists.

The locality at which the silver ore is said to have been found is at a place called Boorook in New South Wales, near to the borders of Queensland. A specimen of the ore was shown to me on the 24th of December, 1877. The particular piece in question consisted of a dark iron-grey coloured highly-granular galena, broken up by veins of what appeared to be pure chloride of silver. As I was very busy at the time, preparing to start for England by the mail steamer leaving that afternoon, I had no opportunity to make any further examination of the specimen, and cannot say whether bromine or iodine was also present or not. The veins of chloride of silver were comparatively thick, perhaps as much as $\frac{1}{3}$rd of an inch in parts.

Since my return to England I have seen several notices in the Colonial newspapers, stating that the deposits are both rich and extensive, and that they will rival those of Nevada. On my return to Sydney I will send you any trustworthy information that I can gather upon the subject.

Yours very truly,
A. LIVERSIDGE.

To Dr. Percy, F.R.S.,
Royal School of Mines.

SILVER AND MERCURY.

At p. 177 insert the following note at the end of the first paragraph:—

By filtering through chamois leather about 10 kilogrammes of argentiferous mercury, which had probably been obtained in 1832, E. Dumas found that some crystals were left on the filter, consisting of 27·4% of silver and 72·6% of mercury. The formula AgH^3 [Ag^2H^4] requires 26·5% of silver and 73·5% of mercury. (Jahresber. for 1869, p. 291, quoted from the Comptes rendus, 69. p. 759.)

Silver and Platinum.

Insert the following note at the end of the article on the alloys of these metals at p. 182:—

An alloy of silver and platinum was used by dentists for pivots of artificial teeth before 1835, as it is mentioned by Chaudet in his "L'Art de l'Essayeur" (p. 378), which was published in that year. He states that the mode of preparation and the proportions of this alloy are unknown; and that dentists seemed to prefer it to alloys of copper and palladium, and of silver and palladium.

Silver and Tin.

At p. 183, after the article on Silver and Tin, insert the following note:—

Tin containing a little silver, and in a peculiar state like tin which has been disintegrated by exposure to extreme cold, is said to be used by dentists for stopping teeth.

Silver and Cadmium.

Insert at p. 171 the following note after the article on Alloys of Silver, Copper, and Zinc:—

I have been informed that an alloy of silver and cadmium is used for the graduated scales on philosophical instruments. It is said to consist of 80% of silver and 20% of cadmium, but an analysis of it by Mr. Richard Smith gave the following composition per cent.:—

Silver	86·66
Cadmium	13·34
Copper	0.02
Gold	0·02
	100·04

Note from Dr. Sterry Hunt on Silver Islet.

Insert the following note at p. 519:—

"Montreal, *Nov.* 18, 1878.

"Dear Dr. Percy,

"As you were curious to learn somewhat more of the Silver Islet Mine, I write to say that I have just seen a trustworthy person lately from the region, who tells me that drifts a few fathoms from the old shaft have disclosed a parallel lode, which has been struck at various points at from 10 to 50 fathoms, at which latter depth a winze is sunk to some distance upon it. The yield from this new lode has enabled them to pay off in the last six months a debt of $400,000, and the weekly yield is now from $50,000 to $70,000. On Nov. 1 the estimated amount in sight was $1,000,000, so that the future of the mine promises well.

"In two other mines near by, which I examined six years since, there have lately been found masses of rich ore, and next year bids fair to see a revival of excitement in that region.

"Very faithfully yours,

"T. Sterry Hunt."

Mints in Australia.

I was informed (June 28, 1878) by my friend Sir William Drummond Jervois, Governor of South Australia, that he knew positively that both the Sydney and Melbourne Mints were then in operation, which he considered to be a great mistake.

Note on the Liquation of Hard Lead.

As it is not improbable that some of the purchasers of this volume may possess the volume on the Metallurgy of Lead, which I published in 1870, I take this opportunity to correct a rather important error in the latter volume on the subject of the Liquation of Hard Lead. The specimen described at p. 467 as the product of liquation was obtained not by that process but by smelting hard lead, and various residual substances containing lead, in admixture with poor coppery regulus, in order to separate copper from the hard lead. The product in question consisted of three layers, having the following physical characters respectively: a top layer (*a*), ¼″ thick, brownish black, dull, like tarnished arsenic in appearance, and wrinkled on the surface; it was easily separable from the next layer,—a second layer (*b*), about ⅓″ thick, crystalline, granular, somewhat resembling pig-iron in structure, metallic in lustre, and having the colour of antimony,—and a third layer (*c*), about 2½″ thick, largely crystalline, foliated, of a bright metallic lustre and of the colour of antimony: here and there in this layer there were crystals similar in appearance to those forming the second layer (*b*).

The analysis of the third layer (*c*) is given on p. 468 of the volume on the Metallurgy of Lead. The top layer (*a*) was analysed in my laboratory by the late W. J. Ward, in 1870, and found to have the following composition per cent.:—

Lead	42·22
Iron	19·39
Copper	11·15
Antimony	4.93
Sulphur	21·41
	99·10

This substance was, consequently, a regulus.

To form sulphide of lead,	42·22 of lead	require	6·49	of sulphur.
Do. ferrous sulphide,	19·39 of iron	do.	11·08	do.
Do. cuprous sulphide,	11·15 of copper	do.	2·78	do.
Do. sulphide of antimony,	4·93 of antimony	do.	1·13	do.
		Sulphur calculated =	21·48	
		Do. found =	24·41.	

END OF PART I. ON THE METALLURGY OF SILVER AND GOLD.

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[This Index has been prepared by Mr. THOMAS W. NEWTON, Assistant Librarian of the Museum of Practical Geology.]

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THE

ROYAL SCHOOL OF MINES

AND THE

SCIENCE AND ART DEPARTMENT.

LETTER FROM DR. PERCY TO THE 'MINING JOURNAL.'

[*Reprinted from the 'Mining Journal,' Jan.* 3, 1880.]

TO THE EDITOR.

SIR,—On the 9th inst. I resigned the Lectureship on Metallurgy at the Royal School of Mines, to which I was appointed in 1851 by the Duke of Somerset, then First Commissioner of Her Majesty's Works and Public Buildings, the School having been founded in that year in connection with the Museum of Practical Geology in Jermyn Street. Although I am not vain enough to suppose that my retirement from the school is of itself a circumstance either interesting or important to the public, yet I think I shall be able to show that it involves considerations which, in a national point of view, are neither uninteresting nor unimportant.

A school of mines is essentially a technical school. Its special object is to impart a knowledge of the principles of mining, or, what is equivalent, a knowledge of the science of the art of mining. Every art has a science of its own. An art can only be acquired by practice, so that in order to become a miner or a mine agent a man must have personal experience in mining. The science of mining is of a complex nature, and amongst its components may be mentioned mechanics, hydro-dynamics, mineralogy, and geology.

In former times, in the case of metalliferous mining, it was the practice to extract the metal at or near the mines, and at present also, in many localities, the same practice continues. Hence arose the connection between mining and metallurgy, the latter being the art of extracting metals from their ores. For this reason, in every school of mines instruction in metallurgy has accompanied that in mining. Metallurgy, like mining, can only be taught theoretically in schools, excepting one branch of it—assaying, which is the art of finding by ready methods the proportion of metal in an ore or other substance. A student may in a mining school acquire as much skill in assaying as in metallurgical works, and become, therefore, qualified on leaving the school to practise this art as a means of livelihood.

From what I have advanced it will be perceived that the student at a school of mines should possess some knowledge of certain sciences of a general character, which may be designated preliminary

knowledge, in order to qualify him for receiving instruction in the specific technical part of the teaching—mining and metallurgy. To this point I beg to direct particular attention, as it appears to me to be one of paramount importance. The preliminary knowledge may be obtained at various excellent institutions in London and the country, of which I may name University College and King's College, London, and Owens College, Manchester. Indeed, I may add that it is not obligatory on a student of the Royal School of Mines to attend, for example, the courses of chemistry and physics delivered at that School, though he must submit to be examined in those subjects by the lecturers of the School. This I have always considered to be unjust, and, in my opinion, certificates of competency from the teachers of such colleges as the above-named should suffice for the Royal School of Mines.

It would occupy too much space to give a detailed account of the history and progress of the Royal School of Mines. All these details are contained in a pamphlet which I have printed, but not yet published, and which, with additions, I propose hereafter to publish. I may refer also to a letter from myself, containing similar information, which appeared in the *Times* of August 24, 1871. It will suffice in this communication to state only the following particulars. A geological survey of the United Kingdom of Great Britain and Ireland having been commenced, it was decided to preserve and permanently exhibit in a public national museum specimens of the fossils, rocks, ores, and other mineral substances which it became necessary to collect and examine in the course of that survey. At first the collection found a home in a house in Craig's Court, Charing Cross, where the accommodation was wholly inadequate. It was transferred to the beautiful Museum in Jermyn Street, which owes its existence to the late Sir Robert Peel, at the instigation of one of the most illustrious and energetic geologists of the day—the late Sir Henry de la Beche—whose premature death was a heavy loss to the Museum. The Museum was formally opened on May 12, 1851, by the late Prince Consort, who, in answer to an address from Sir H. de la Beche, expressed himself warmly in its favour. (See the report of the Prince's speech in the *Times* of May 13, 1851.) There was then no dream of an omnivorous South Kensington octopus. It was next determined to utilize the collection by making it subservient to teaching, and so arose the School of Mines, which was established as an integral part of the Museum. It should also be stated that petitions to the Government in favour of this course came from all the great mining districts of the country. Models illustrative of practical geology, mining, and metallurgy, as well as specimens illustrative of metallurgical processes, were added from time to time; and a Mining Record Office, for the preservation of plans of mines—with a view to the saving of life and property—and for procuring and compiling mineral statistics, completed the scheme.

The Geological Survey, the Museum, and the School of Mines were, as I have intimated, at first under the management of the Office of Works; they were next transferred to the Board of Trade, and

finally to the Education Department, after the birth of what is called the Science and Art Department. Not long afterwards, through influence well known to many persons, but which it would be indiscreet to publish, the Royal College of Chemistry, at that time in a bankrupt state, was attached to the School of Mines, and even the name of the School was changed to that of Metropolitan School of Science applied to Mining and the Arts. This step proved unfortunate; the confidence of the mining interest in the School was shaken, and it became necessary to revert to the original title, with the substitution of "Royal" for "Government" School, the School having originally been designated the Government School of Mines. By slow degrees the confidence of the mining interest in the School was restored, and at length it attained what appeared to be a secure position, and annually attracted numerous students.

The trials of the School were not yet over. A Royal Commission on Scientific Instruction was appointed some years ago, and one of its recommendations was the removal of the School to South Kensington, to be there merged in the general science teaching, and so lose its individuality. This recommendation was warmly resisted by the late Sir Roderick Murchison, then Director of the Geological Survey, of the Museum, and of the Royal School of Mines, and by those of its lecturers on the special and really technical subjects of the curriculum. A similar recommendation was made by the Commissioners respecting the School of Naval Architecture, which, in my opinion, the Government wisely did not adopt; the School, which had been formed and originally located at South Kensington, having been transferred to Greenwich Hospital. Now I come to that part of the subject which specially concerns the metallurgical branch of the Royal School of Mines, which until recently I had the honour and pleasure of directing.

The Museum is built on Crown land, and the houses adjoining on each side, up to St. James's Church on the west, and Eagle Place on the east, are also on Crown land. The metallurgical laboratory of the School is contiguous to the Museum on the east, and includes the basement of a house in the occupation of the Department of Science and Art, the upper part of which is devoted to officers of the palæontological staff of the Geological Survey. About two years ago the leases of the block of houses on the east expired, and the land on which they are situate was leased by the Office of Woods (which acts as land agent for the Crown estates, while the Office of Works maintains the public buildings erected thereon) to a building company. But previously the Office of Works had reserved a plot for a new metallurgical laboratory, for which the ground rent to the Crown would have amounted only to a trifling sum. A plan of the plot was made, which I delivered to Lord George Hamilton, Vice-President of the Council; and by every argument I could adduce, both at a personal interview with his lordship and in letters, I entreated him to use his influence to keep the laboratory in its present locality. Further, I twice, in conversation with his lordship, offered to build a laboratory on the site of the existing one at my own cost,

and present it to the nation, sooner than have it removed to South Kensington. My arguments proved unavailing. I received a letter from the Education Department, dated on the very day on which Parliament was last prorogued, informing me that the Lords of the Committee of Council on Education had decided to remove the metallurgical department of the School to South Kensington at Christmas, actually during the course of a session, which would obviously cause great inconvenience. There was no necessity for this hurry, because the laboratory and house contiguous to the Museum will remain idle in the occupation of the Office of Works till October 1880.

At that season of the year it would have been useless to offer opposition, as the heads of the Education Department were out of town. I, therefore, waited for an opportunity of addressing the Chancellor of the Exchequer on the subject. To him I appealed against the decision of the Committee of Council, a decision which I feel confident would be all but unanimously condemned by the great mining and metallurgical interests of the country; and having received a proposal from the building company, before mentioned, to provide me with a suitable laboratory somewhat larger than the present one at a rent of 300*l.* per annum, or one twice the size at a rent of 500*l.*, I offered to conduct the laboratory free of expense to the Government—in fact, to make it wholly instead of nearly self-supporting as it was, accompanying the offer with a promise to give ample security to the Treasury for the fulfilment of this undertaking. The only answer which the Chancellor of the Exchequer gave was that such an application was not in accordance with official rules, and he referred me to the Committee of Council, against whose decision I had appealed to him. Almost immediately after receiving this answer I resigned the Lectureship on Metallurgy at the Royal School of Mines, offering at the same time to complete the present course of lectures, but only on the condition of being allowed to do so in the Museum in Jermyn Street, and stating that under existing circumstances I was convinced I could not do justice to the students except within the precincts of the Museum—an offer which has been declined. It will naturally be asked why I objected to the removal of the metallurgical department of the Royal School of Mines from its present locality to South Kensington. The answer will be found in the pamphlet which I have previously referred to. But I will here state as concisely and clearly as I can on what I found my chief objections.

I object to the removal, because of its destroying the connection with the Museum of Practical Geology, rich in illustrative models and specimens, which are admirably displayed in glass cases for the use of students. It is not, I believe, at present proposed to rob the Museum of these valuable illustrations—a robbery which would, if I mistake not, be loudly protested against by a not uninfluential part of the community. I object to the removal, because the associations, I venture to assert, of all the really mining students past and present of the School are connected with the existing institution. These students are scattered far and wide throughout the kingdom and many foreign countries, and on their coming to London they have

rarely failed to visit the old scene of their studies, and to express their attachment to it. I do not mean to say that circumstances might not occur which would necessitate such a removal, but I affirm that there is no such exigency at present. It may be alleged that this objection is sentimental in its nature. Be it so. What force, I should like to know, operates more powerfully on mankind than sentiment? and no wise statesman ever ignores it. I object to the removal, because I believe it will destroy the individuality of the School of Mines by mingling its purely technical instruction with what is called general instruction in science, and I feel sure that all the graduates and students of the School are opposed to this submergence (for such it is) of the School.

One argument in favour of the removal of the Metallurgical Department of the School to South Kensington will, I anticipate, be founded on the fact that four of its lecturers have already been transferred to that quarter. The subjects of those four lecturers are natural history, chemistry, physics, and geology, from which it will be seen that, excepting geology, the essential, purely technical portion of the instruction is still imparted in the original locality in Jermyn Street. I say still, for the labours of my successor, whoever he may be, will not commence at South Kensington until Jan. 5 next, and possibly not even then.

I will deal with this argument in opposition to the views which I and others advocate. Natural history was the first to depart to South Kensington, and to depart voluntarily—not, as in my case, under compulsion. One of the reasons assigned for this step was the want of space in the Museum in Jermyn Street for a "Biological Laboratory," a modern euphuism for dissecting-room. I was not sorry to witness the departure of natural history; for however eminent its expositor may be, it is a subject which ought never to have formed part of the curriculum of the Royal School of Mines, and into no other mining school in the world has such a lectureship been admitted. Although I yield to no man in a love for natural history, and in a desire to see a knowledge of it diffused through all classes of society, yet my opinion is that the lopping off that branch of study from the School would be a great gain rather than a loss. In this opinion men practically acquainted with mining and metallurgy unanimously, I believe, agree with me. It was only a few days ago that one of the foremost of our civil engineers said to me, "I never could understand why natural history formed part of the course of instruction at your School of Mines;" on which I remarked, "Nor I either."

With regard to the location of the courses of instruction in chemistry, physics, and mechanics at South Kensington, the Royal School of Mines, I believe, suffered no loss by their removal. They form part of general science teaching, which the Department of Science and Art has taken under its fostering wing. The line of demarcation between them and the purely technical subjects of the teaching at a school of mines is perfectly definite. What is wanted

at the Royal School of Mines are competent instructors in mine surveying, and in mining and metallurgical machinery, if peradventure such can be procured, which I much doubt, at stipends of 200*l.* per annum each.

When geology left Jermyn Street, in the person of the youngest lecturer at the Royal School of Mines, I felt some regret, but was consoled by the reflection that a sound knowledge of theoretical geology could be easily obtained by the study of such admirable works as Lyell's "Principles of Geology," and that for many years practical instruction in that part of geology most useful to miners—palæontology—had been given by one of the most practical and able living palæontologists—Mr. Etheridge—who, I am glad to say, remains still attached to the Museum.

I delighted always in the performance of my duty, and rejoice to think that I number many of my old students amongst my best friends. From them I have ever received the warmest sympathy and information of the greatest value in the preparation of the volumes on Metallurgy which I have written and published, and which contain 3500 octavo pages. I hope still to continue to receive communications from them which may aid me in the completion of the task of my life—the production of a series of volumes containing all that is known in metallurgy up to the present day.

As my connection with the Royal School of Mines has for ever ceased, I have no personal object in making the following concluding remarks. The Education Department has, I think, contrary to its intention, made a fatal mistake in the course it has taken; it has shaken public confidence in the Royal School of Mines, which I fear may never be restored, and it has irritated the graduates and students of the school, every one of whom, it should be remembered, is a living advertisement. To complete the work of destruction only one step more remains to be taken, and that is to remove the instruction in mining to South Kensington. I personally count for nothing in this matter. My contention has been for a principle, the value of which the public will one day appreciate—the principle opposed to excessive centralization, to absorption, and to the extinction of individual vitality.

JOHN PERCY, M.D., F.R.S.

Gloucester Crescent, Hyde Park,
Dec. 29, 1879.

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